

# DEVELOPMENT OF SUPPORTED POLYMERIC LIQUID MEMBRANE TECHNOLOGY FOR AQUEOUS MTBE MITIGATION

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*Prepared By:*

**Electric Power Research Institute**

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***Prepared By:***

Electric Power Research Institute (EPRI)  
3412 Hillview Avenue  
Palo Alto, California 94304  
Contract No. 100-98-001

***Prepared For:***

**California Energy Commission**

Gary Klein  
***Contract Manager***

Terry Surles

***Program Manager***  
**Public Interest Energy Research Program**

Marwan Masri

***Deputy Director***  
**Technology Systems Division**

Robert L. Therkelsen

***Executive Director***

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# **Development of Supported Polymeric Liquid Membrane Technology for Aqueous MTBE Mitigation**

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## **Cosponsors:**

Public Interest Energy Research Program (PIER)  
California Energy Commission  
1516 Ninth Street  
Sacramento, California 95814

## **PIER Project Manager**

P. Kulkarni

EPRI

3412 Hillview Avenue  
Palo Alto, California 94304

## **EPRI Project Managers**

K. Amarnath  
A. Michel

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**Spectrum Laboratories, Inc.  
Bren School of Environmental Science & Management**

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# CITATIONS

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This report was prepared by

Spectrum Laboratories, Inc.  
18617 Broadwick Street  
Rancho Dominguez, CA 902

Principal Investigator  
J. Martinez

Bren School of Environmental Science & Management  
University of California, Santa Barbara  
Santa Barbara, California 93106

Principal Investigator  
A. Keller

This report was prepared for

EPRI  
3412 Hillview Avenue  
Palo Alto, California 94304

and

Public Interest Energy Research Program (PIER)  
California Energy Commission  
1516 Ninth Street  
Sacramento, CA 95814

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# REPORT SUMMARY

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The use of MTBE (Methyl tert-Butyl Ether) as a gasoline additive has generated a serious, widespread groundwater contamination problem in California. This study evaluated the use of supported polymeric liquid technology membrane technology in the remediation of MTBE contaminated groundwater.

## Background

In addition to the currently investigated technologies for removal and/or destruction of MTBE in groundwater, such as oxidation, air stripping and activated carbon adsorption, membranes could provide an effective cost competitive means for this treatment. The key issue will clearly be that of economics: the process has to be cost effective, as well as practical on a large scale. A recent development in membrane technology, supported polymeric liquid membranes, introduces great flexibility by significantly enhancing membrane transport rates and thus driving down the cost. The diversity of MTBE contamination situations, which range from levels at low ppb to thousands of ppm, will require combination of complementary technologies to achieve the best economical approach for each situation. Membranes could play a key role in this combined approach, especially at high ppm levels, because they work by removing a constant fraction of the initial contaminant level. The same amount of membrane area and thus the same cost will remove the same percentage of the initial contaminant amount, whether it is 1% or 0.01%.

## Objectives

To develop and demonstrate the effectiveness of a new liquid membrane technology for the reduction and removal of MTBE contaminant in California water supply.

## Approach

In work cosponsored by the California Energy Commission, the project team evaluated two important factors in the development of a supported polymeric liquid membrane process for removal of MTBE from contaminated water: selection of the liquid polymer and evaluation of a hollow fiber module. In the selection of the liquid polymer, the team measured the MTBE transport rate of polybutylene glycol 4800 (PBG-4800) and Silicone 350 (Si-350), the two most promising polymers for this application. After selecting Si-350 as the preferred liquid polymer, the team used a small bench-scale hollow fiber membrane to test the removal of MTBE from water and establish the effects of membrane structure (porosity, pore size and wall thickness) on system performance (liquid membrane stability and transport rates). In a subsequent phase of the research, the team conducted comparative studies of Liquid-Polymer Impregnated Hollow Fiber Membranes (LP-HFM) in two configurations: (1) a conventional construction with the fibers potted longitudinally within the membrane module, resulting in tangential flow, and (2) an

experimental design with the fibers wound around a central perforated shaft, resulting in axial flow.

## Results

The membranes studied in this research have pores filled with Si-350, a polymeric liquid with an affinity for MTBE. The membranes are formed into hollow tubes and assembled into modules so that contaminated water flows through the lumen of the tubes while air or some other gas flows over the outside surface. Two module designs were tested, one with longitudinally arranged fibers and one with fibers wound around the central shaft like kite twine.

Tests indicate that MTBE can be readily removed from the solution using supported polymeric liquid membranes impregnated with Si-350. The removal rate of MTBE, as measured by the mass transfer coefficient,  $K_{oL}$ , is a function of liquid flow rate and almost independent of the gas flow rate under the conditions tested. In general,  $K_{oL}$  for the tangential flow membranes was 25% higher than for the axial flow membranes, possibly due to the current flow pattern, which might not result in effective use of the entire membrane surface area. Given the relatively short expected life of the membranes (one to three years), the overall cost of treating water contaminated with MTBE using LP-HFM is currently estimated to be 6-10 times higher than other treatment processes such as granular activated carbon (GAC) or air stripping. Even if the membranes were used in combination with a GAC polishing step, the overall cost of treatment would be 4-8 times higher than GAC alone.  $K_{oL}$  would have to increase by a factor of 15-20 to result in a cost competitive process. Alternatively, the life of the membrane would have to increase to more than 20 years to result in a cost competitive process.

## EPRI Perspective

Further research is warranted to determine whether the cost barriers to the use of LP-HFM for MTBE removal can be overcome. Specific research issues to address are:

- Improving the flow of water through the membranes to make full use of the membrane surface area, which will significantly improve overall MTBE mass transfer to the gas phase
- Developing a less expensive membrane
- Determining the life expectancy of the membranes under accelerated test conditions

## Keywords

Supported polymeric liquid membrane  
MTBE (Methyl tert-Butyl Ether)  
Volatile organic chemicals (VOCs)  
Groundwater protection  
Environmental remediation



# ABSTRACT

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Development of Supported Polymeric Liquid Membrane Technology (trademarked by Spectrum Laboratories, Inc. as SeleXtrac<sup>TM</sup>) for Aqueous MTBE Mitigation

The majority of membrane applications that involve aqueous solutions are based on molecular size differences, ionic charge and pore size to achieve the desired separation. These applications expand the range from small molecules to protein size compounds. Molecular separation by size or charge exclusion has many shortcomings. There has been a clear need to achieve separation of molecular entities based on the properties of the dissolved compounds in addition to size or charge. This concept has been employed in an approach called SeleXtrac<sup>TM</sup>, supported polymeric liquid membrane in which membrane transport is facilitated by impregnating a polymeric (oligomeric) liquid that resides (is supported) within the pores of a microporous membrane and which has a high affinity for the compound of interest. One unique application of SeleXtrac<sup>TM</sup> is treating aqueous wastes discharged from chemical plants that typically contain low levels of organics and where conventional membrane separation is inadequate and inefficient. The selective extraction and recovery of relatively hydrophobic volatile organic (VOC's) compounds can be obtained by using these liquid membranes. In controlled experiments, we have used SeleXtrac<sup>TM</sup> to study the effectiveness and cost reduction implications of this technology to remove MTBE (Methyl Tertiary Butyl Ether), a widespread contaminant of groundwater in the state of California.

The results indicate that MTBE can be readily removed from a solution using SeleXtrac<sup>TM</sup> technology when the membrane pores are impregnated with a silicone polymer (Si-350) and in a pervaporation mode. The results also showed that the projected cost of treating water contaminated with MTBE was 6-10 times higher when compared to other treatment technologies such as granular activated carbon (GAC) or air stripping; 4-8 times higher if combined with GAC polishing steps than for GAC alone. The projected high cost is due to membrane module cost and unknown life expectancy, which led us to use very conservative estimates. Further studies would be highly beneficial to determine the feasibility of developing less expensive, more efficient and durable SeleXtrac<sup>TM</sup> modules. Such modules could be tested under accelerated test conditions in an attempt to overcome the cost barriers to the use of this technology to remove MTBE and many other organics from contaminated water.



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# 1

## EXECUTIVE SUMMARY

---

The use of MTBE (Methyl tert-Butyl Ether) as a gasoline additive has generated a serious, widespread groundwater contamination problem in California. This study evaluated the use of supported polymeric liquid membrane technology (trademarked by Spectrum Laboratories as SeleXtrac<sup>TM</sup>) in the remediation of MTBE contaminated groundwater. This project was co-sponsored in part by the California Energy Commission (CEC) and supports the Public Interest Energy Research (PIER) Program objective of improving the value of electricity, and improving the environment and public health costs/risks of California's electricity by developing energy efficient clean-up technologies for removing MTBE and other organic contaminants from the environment, reducing human and ecological exposure to these contaminants.

In addition to the currently investigated technologies for removal and/or destruction of MTBE in groundwater, such as oxidation, air stripping and activated carbon adsorption, membranes could provide an effective cost competitive means for this treatment. The key issue is clearly economics: the process has to be cost effective, as well as practical on a large scale. SeleXtrac<sup>TM</sup>, a recent development in membrane technology, supported polymeric liquid membranes, introduces great flexibility by significantly enhancing membrane transport rates and thus driving down the cost. The diversity of MTBE contamination situations, which range from levels at low ppb to thousands of ppm, will require a combination of complementary technologies to achieve the best economical approach for each situation. Membranes could play a key role in this combined approach, especially at high ppm levels, because they work by removing a constant fraction of the initial contaminant level. The same amount of membrane area and thus the same cost will remove the same percentage of the initial contaminant amount, whether it is 1% or 0.01%.

The objective of this project was to focus on the development of advanced technology for the removal and mitigation of MTBE as a source of contamination of potable water. The approach employed cutting edge SeleXtrac<sup>TM</sup> Liquid Membrane Technology co-acting with hollow fiber membranes modules specially configured with an advanced axial geometric layout of hollow fiber microporous membranes simulating a kite string spooling arrangement. The unique geometry of the hollow fiber arrangement and the presence of the liquid polymer within the pores of the membrane was considered to be an energy and cost efficient approach to the removal of MTBE contaminant from ground water.

The project team evaluated several important factors in the development of a supported polymeric liquid membrane process (SeleXtrac<sup>TM</sup>) for removal of MTBE from contaminated water: design, construction and testing of a three-channel spinneret; determine the best chemical composition to spin new hollow fibers; spin hollow fibers with the appropriate physical characteristics including pore size; design and construction of axially wound hollow fiber

modules; selection of the liquid polymer and construction of hollow fiber modules (tangential vs. axial flow geometry). In the selection of the liquid polymer, the team measured the MTBE transport rate of polybutylene glycol 4800 (PBG-4800) and Silicone 350 (Si-350), the two most promising polymers for this application. After selecting Si-350 as the preferred liquid polymer, the team used a small bench-scale hollow fiber module to test the removal of MTBE from water and establish the effects of membrane structure (porosity, pore size and wall thickness) on system performance (liquid membrane stability and transport rates). In a subsequent phase of the research, the team conducted comparative studies of SeleXtrac<sup>TM</sup> Membranes in two configurations: (1) a conventional construction with the fibers potted longitudinally within the membrane module, resulting in tangential flow, and (2) an experimental design with the fibers wound around a central perforated shaft, resulting in axial flow. Overall mass transfer coefficients were determined, which are the basis for design and up scaling. Preliminary cost and energy calculations were conducted to estimate the overall removal cost under various scenarios.

The SeleXtrac<sup>TM</sup> membranes tested in this study have pores filled with Si-350, a polymeric liquid with an affinity for MTBE. The membranes are formed into hollow tubes and assembled into modules so that contaminated water flows through the lumen of the tubes while air or some other gas flows over the outside surface. Two module designs were tested, one with longitudinally arranged fibers and one with fibers wound around the central shaft like kite twine.

Tests indicate that MTBE can be readily removed from the solution using supported polymeric liquid membranes impregnated with Si-350. The removal rate of MTBE, as measured by the mass transfer coefficient,  $K_{oL}$ , is a function of liquid flow rate and almost independent of the gas flow rate under the conditions tested. In general,  $K_{oL}$  for the tangential flow membranes was 25% higher than for the axial flow membranes, possibly due to the current flow pattern, which might not result in effective use of the entire membrane surface area. Given the relatively short estimated life of the membranes (one to three years), the overall cost of treating water contaminated with MTBE using SeleXtrac<sup>TM</sup> is currently estimated to be 6-10 times higher than other treatment processes such as granular activated carbon (GAC) or air stripping. Even if the membranes were used in combination with a GAC polishing step, the overall cost of treatment would be 4-8 times higher than GAC alone. There is little or no information about the actual life of the membranes under this application, so the estimate might be very conservative.  $K_{oL}$  would have to increase by a factor of 15-20 to result in a cost competitive process, or the cost of the membranes would have to be reduced by a similar proportion.. Alternatively, the life of the membrane would have to increase to more than 20 years to result in a cost competitive process. The solution probably lies in a combination of these three factors: increased mass transfer, lower unit cost and longer life.

Regarding the energy consumption of this technology as compared to various other technologies, the project team evaluated energy consumption of various alternative technologies. In conclusion, the GAC system would require the least energy, mostly to pump the contaminated water through the bed of activated carbon. This is followed by air stripping, which considers both the pumping of water to the top of the column and the air blower used to bubble in air for the VOC stripping process. The membrane systems would be slightly above air stripping, mainly due to the significant membrane area required to perform the separation of MTBE from water

using the SeleXtrac™ systems. The energy consumption of the membrane systems are likely to decrease as more efficient membrane designs are developed.

Further research is warranted to determine whether the cost barriers to the use of SeleXtrac™ membrane modules for MTBE removal can be overcome. Specific research issues to address are:

- Improving the flow of water through the membranes to make full use of the membrane surface area, which will significantly improve overall MTBE mass transfer to the gas phase
- Developing a less expensive membrane
- Determining the life expectancy of the membranes under accelerated test conditions.



# 2

## INTRODUCTION

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### I. BACKGROUND ON MTBE CONTAMINATION AND TREATMENT

The use of MTBE as a gasoline additive has generated a serious, widespread groundwater contamination problem in California. Methyl tert-Butyl Ether (MTBE) as well as a number of other organic contaminants (e.g. ethers, solvents, aromatic hydrocarbons) in groundwater, surface water and industrial water effluents, present significant challenges in terms of water treatment due to their physicochemical characteristics. The primary source of contamination in groundwater is leaking underground fuel tanks (LUFTs). There are thousands of such sites in California, some resulting in nearby groundwater concentrations of MTBE as high as 5,000,000 ppb. MTBE in groundwater migrates from the LUFTs to drinking water supplies. As a reference the current secondary Maximum Contaminant Level (MCL) determined by the California Department of Health Services for MTBE in drinking water is 5 ppb, while the primary MCL is 13 ppb. The challenge is thus to remove large amounts of MTBE from contaminated water supplies or effluents.

The problem is compounded by MTBE's relatively high solubility, low Henry's constant (Bierwagen and Keller 2000), low sorption or low biodegradability. Common treatment technologies such as air stripping, granular activated carbon (GAC) or bioremediation are not very cost-effective (Keller, Sandall et al. 1998; Keller, Sandall et al. 2000). A common problem with current technologies is the affinity of MTBE and other relatively hydrophilic organic compounds for the aqueous phase, requiring innovative approaches to separate them from water. Oxidation using ozone, ozone/hydrogen peroxide or UV/hydrogen peroxide has so far been limited due to the relatively high cost of these treatment technologies (Mitani, Bunton et al. 2000). Studies using Hollow Fiber Membranes (HFM) under pervaporation indicate that this is a viable option for removing MTBE from an aqueous solution (Keller and Bierwagen 2001).

Prior studies (Keller, Sandall et al. 2000) on the removal of MTBE using a number of conventional and innovative treatment technologies indicated that the choice of technology depends to a significant extent on liquid flowrate, initial concentration and the need to treat any effluent streams (e.g. MTBE vapors, GAC contaminated with MTBE). Air stripping is a very competitive technology at high liquid flowrates, unless air treatment is required. At lower flowrates, HFM has the potential for being a very competitive technology, in particular since the contaminated air flowrate associated with HFM is much smaller than with air stripping. Competing technologies are Advanced Oxidation Processes, namely ozone/hydrogen peroxide or ozone/UV oxidation. As indicated in more detail in Keller et al. (2000) and Mitani et al. (2001), the concern is the production of oxidation intermediates such as tert-butyl alcohol and/or other oxidation byproducts such as bromate from bromine in the water matrix.

Microporous HFM have been successfully used to strip various compounds from water such as Volatile Organic Compounds (VOCs), hydrogen sulfide, sulfur dioxide, oxygen, carbon dioxide, bromine, and ammonia using a sweep gas to remove the gases and vapors from the membrane surface (Zhang and Cussler 1985; Zhang and Cussler 1985; Yang and Cussler 1986; Semmens, Qin et al. 1989; Zander, Semmens et al. 1989; Semmens, Foster et al. 1990; Sarti, Gostoli et al. 1993). HFM improves the mass transfer rate of dissolved VOCs from water to air. Contaminated water is pumped through the lumen side of bundled microporous hydrophobic hollow fibers while a vacuum is drawn counter-currently on the outside of the fibers. The hydrophobic membrane allows for efficient transfer of volatile compounds from aqueous to gas phase. While the water is pumped through the hollow fibers, volatile components volatilize and diffuse through the gas-filled pores of the hollow fiber, due to the large concentration gradient. Volatile compounds can then be pulled through by a vacuum and/or swept away by a sweep gas. Pollutants can be effectively transferred through the gas-filled pores to the gas phase while water does not permeate due to the polymer's hydrophobic nature. Hollow fibers have a large surface area per unit volume, allowing greater contact between the phases. This provides relatively fast removal of the contaminant. Studies by (Semmens, Qin et al. 1989) and (Zander, Semmens et al. 1989) showed that mass transfer of VOCs could be an order of magnitude greater than achievable by packed tower aeration when using HFM with a sweep gas.

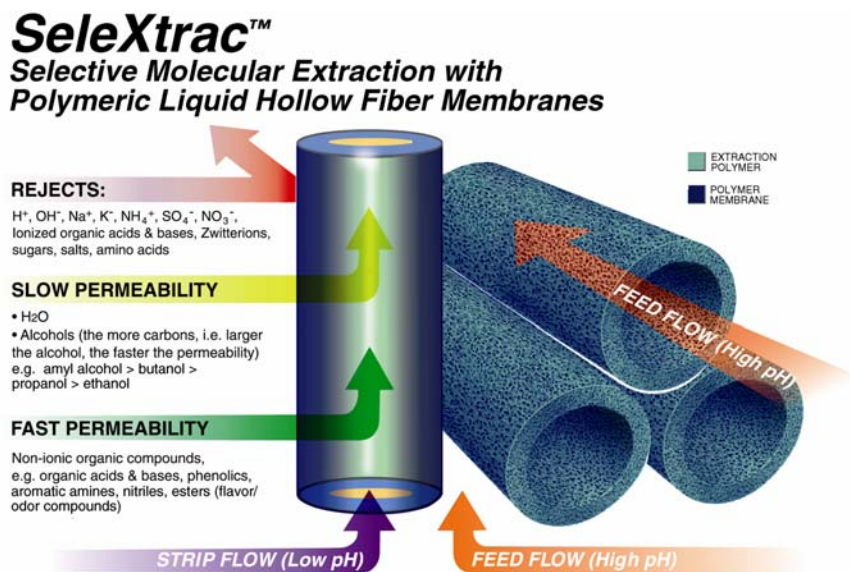
The key issue is clearly that of economics: the process has to be cost effective and practical on a large scale. A recent progress in membrane technology, called "supported polymeric liquid membranes" (SeleXtrac<sup>TM</sup> Liquid Membrane Technology) developed by Monsanto and acquired by Spectrum Laboratories, Inc., introduces great flexibility in significantly enhancing the membrane transport rates, thus driving the cost down substantially. The SeleXtrac<sup>TM</sup> technology accomplishes this by enabling the coupling of the best membrane support structure (porosity, pore size, module geometry and thickness) with an optimum polymeric liquid and controlled coating technology. The SeleXtrac<sup>TM</sup> membranes can have diverse selective separation applications in the biomedical and industrial sector by tailoring the appropriate liquid polymer for a specific molecular extraction. Potential applications include the removal of trace organics from contaminated water (MTBE and other VOCs), recovery of products from process streams (alcohols, acids), flavor recovery from food processing and extractions of specific components for recovery and analysis.

The diversity of the contamination situations, which range from levels at low ppb to thousands of ppm, will require a combination of complementary technologies to achieve the best economical approach for each situation. Membranes could play a key role in this combined approach. For instance, activated carbon adsorption tends to be very efficient at treating organic contaminants at very low levels, since carbon binds tightly to many organics, and the lower the contaminant level the more water volume can be treated for the same amount of carbon. Membranes, however, tend to be more cost effective at high ppm levels, because they work by removing a certain fraction of the initial contaminant level; the same amount of membrane area (thus the same cost) will be required to remove, say, 90% of the initial contaminant concentration, be it 1% or 0.01%.

## II. SELEXTRAC™ LIQUID MEMBRANE TECHNOLOGY

The SeleXtrac™ technology consists of a porous membrane support structure with a polymeric liquid coating the pores. The SeleXtrac™ membranes contain pores of various sizes. The SeleXtrac™ membranes are prepared by filling the pores with polymeric liquids following the polymer loading procedures outlined in Addendum 2.0. The polymer has an affinity or attraction for compounds of interest. When membranes are prepared in this fashion, the membrane's ability to separate compounds from a liquid stream depends primarily on the chemical properties of the liquid polymer used to fill the pores and does not depend on the physical sieving of molecules through the membrane pores.

Figures 2-1 and 2-2 present schematic representations of the SeleXtrac™ technology using hollow fiber membranes. As can be seen in Figure 2-1, the membrane with a polymeric coating rejects most ionic compounds. Water and alcohols can also be selectively excluded by choosing the appropriate liquid polymer, which can have a high permeability for targeted organic compounds in the feed flow. The strip or sweep flow can be a liquid solution (e.g. a low pH solution as depicted in Figure 2-1) or a gas, as used in the current studies.



**Figure 2-1**  
 Schematic representations of the SeleXtrac™ technology using hollow fiber membranes.

**Figure 2-2**

**Schematic representation of a SeleXtrac™ membrane showing the pores of the membrane backbone impregnated with a polymeric (oligomeric) liquid having affinity for an organic compound of interest.**

### **III. OUTLINE OF THE PROJECT**

The project was divided into three phases:



### ***PHASE 1: Polymeric Liquids Selection & Coating Technology***

This phase consisted of two tasks:

1. Screening of existing liquid polymers to optimize transport of MTBE across the membrane, by measuring the partition coefficient for each liquid polymer and the corresponding permeation rate through a standard membrane support.
2. Testing and optimization of the coating process of the liquid polymer selected on the membrane support, with the main criteria being high transport rates and stability.

### ***PHASE 2: Membrane Support and Module Design***

This phase was also divided into two tasks:

1. Design of a multi-channeled spinneret to construct the polymeric hollow fiber supports for the polymeric liquid that would optimize transport rates and stability for wastewater treatment.
2. Design and development of prototype SeleXtrac<sup>TM</sup> membrane modules. The modules were fabricated using: (a) a conventional geometry; and (b) unique axial cross winding spooling geometry that was expected to maximize mass transfer rates two orders of magnitude from the conventional tangential flow geometry. The axial cross winding fabrication approach should reduce the size and manufacturing cost of the membrane modules while it enhances mass transfer performance at a lower energy cost.

### ***PHASE 3: Feasibility Study of Process for MTBE Treatment***

This phase consisted of three tasks:

1. Test a number of conventional geometry membrane modules, to determine the reproducibility of the fabrication process, as well as the influence of operating conditions on the removal of MTBE.
2. Test a number of axial cross-winding membrane modules, to compare the effectiveness of this design against a more conventional geometry. A number of modules were fabricated to determine reproducibility of the manufacturing process.
3. Develop preliminary cost estimates for a number of scenarios, considering various influent concentrations and flowrates, as well as combinations of the SeleXtrac<sup>TM</sup> process with other polishing technologies such as GAC.

The results from these three phases are described in the following sections of the report.



# 3

## SELECTION OF LIQUID POLYMER AND COATING METHOD

---

### I. INTRODUCTION

Based on previous studies with existing commercially available liquid polymers, silicone 350 (Si-350) and polybutylene glycol MW 4800 (PBG-4800) were considered to be the two best polymers selection for the removal of methyl tertiary butyl ether (MTBE) from contaminated water. These polymers are non-toxic, have extremely low solubility in water, and have been shown to be stable as supported liquid membranes in contact with pure water. Quantitatively, two main parameters are typically used to characterize a new liquid polymer with respect to its utility in the supported liquid membrane configuration: the partition coefficient and the mass transport rate.

The partition coefficient,  $K_p$ , is defined as concentration of MTBE in the polymer relative to the concentration of MTBE in water, at equilibrium.  $K_p$  is a direct measure of the polymer's preference for extracting MTBE from water.

### II. LIQUID POLYMER SELECTION

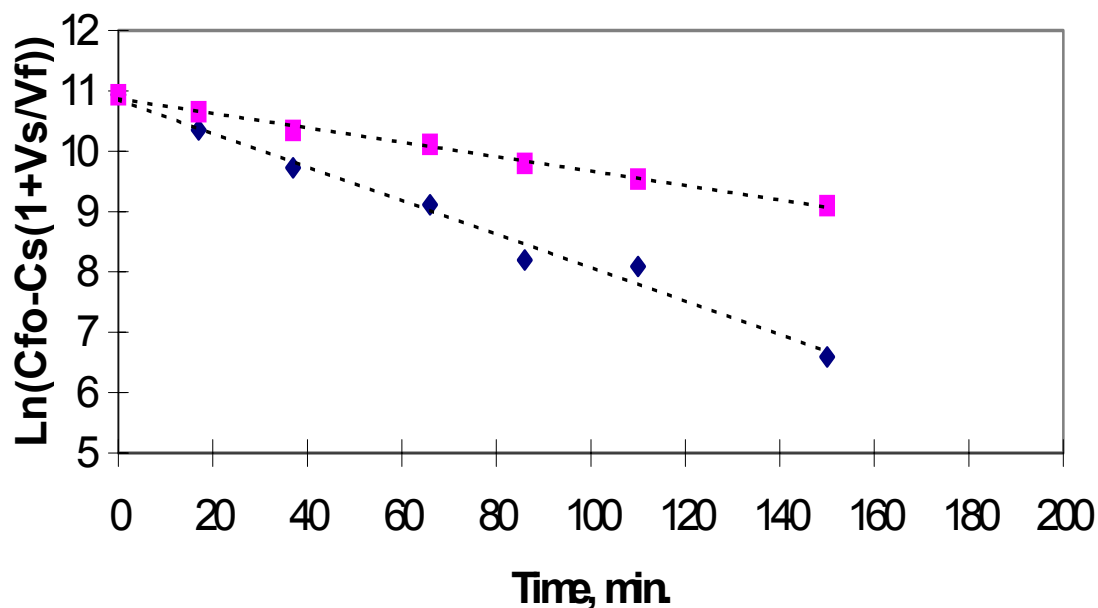
For both polymers at room temperature, the partition coefficient,  $K_p$ , was found to be about 9, which is reasonable considering the high solubility of MTBE in water. For measuring mass transport rates, a standard stirred glass cell with a flat sheet membrane was utilized. This system allows tight control of the membrane preparation, the operating conditions, and an accurate determination of the membrane area.

The mass transport rate test results, in terms of the amounts of MTBE detected in the strip water due to MTBE permeating through the membrane from the feed solution, are shown in Table 3-1. The results show that MTBE accumulated more rapidly in the strip solution for the Si-350 impregnated membrane than for the PBG impregnated membrane. Figure 3-1 shows the fit of a mathematical model for extracting the mass transfer rate,  $K_f$ , from the concentration-time data.  $K_f$  is a quantitative measure of the mass transport rate. As can be seen, the MTBE transport rate with Si-350 is more than two times faster than with PBG-4800 ( $K_f = 9.65 \times 10^{-4}$  cm/s and  $4.24 \times 10^{-4}$  cm/s, respectively).

**Table 3-1**

**Membrane:** liquid polymer in Celgard 2500, area =8 cm<sup>2</sup> **Stirred cell:** top (strip, distilled water, volume = 45 ml) bottom (feed, ~5% MTBE in water, volume = 28 ml).

T = 25°C		Si-350	PBG-4800
Sample	Time, min	MTBE Concentration, ppm	MTBE Concentration, ppm
Initial Feed	0	56000	56000
Strip 1	0	0	0
Strip 2	17	9506	5188
Strip 3	37	15256	9703
Strip 4	66	18514	12382
Strip 5	86	20942	15226
Strip 6	110	21400	17079
Strip 7	150	22758	19371
Feed 7	150	25000	29500



**Figure 3-1**

**Transport of MTBE Across Supported Liquid Membranes Membrane: Celgard 2500 Flat Sheet**

### III. EFFECT OF COATING ON MTBE REMOVAL RATE

With Si-350 selected as the liquid polymer of choice for this application, we studied the use of hollow fiber membrane modules for removal of MTBE from contaminated water. A SeleXtrac™ module (MiniKros Sampler) with a small size and compact design was selected for bench top laboratory testing. The modules were assembled using polysulfone hollow fiber membranes having a 400,000 molecular weight cutoff. The characteristic dimensions of this size module are shown in Table 3-2.

**Table 3-2**  
**Characteristics of the SeleXtrac™ MiniKros Modules**

SeleXtrac™ Module	Active Fiber Length	12.3	cm
MiniKros, PS/400K	Number of Fibers	288	
Shell/Tube Configuration	Fiber ID	0.05	cm
	Fiber OD	0.066	cm
	Fiber Wall Thickness	0.008	cm
	Membrane Porosity	~ 0.5	
	Cross-Sectional Area	0.565	cm <sup>2</sup>

In order to assess the effectiveness of our coating technology, described in more detail in Addendum 2.0, two modules were used. One module was used as a control (uncoated, i.e. membrane pores empty); the other was used as the test module with the pores impregnated with Si-350. Approximately 2.75 g of Si-350 was loaded on the coated module.



**Figure 3-2**  
**Lab System for testing MiniKros modules**

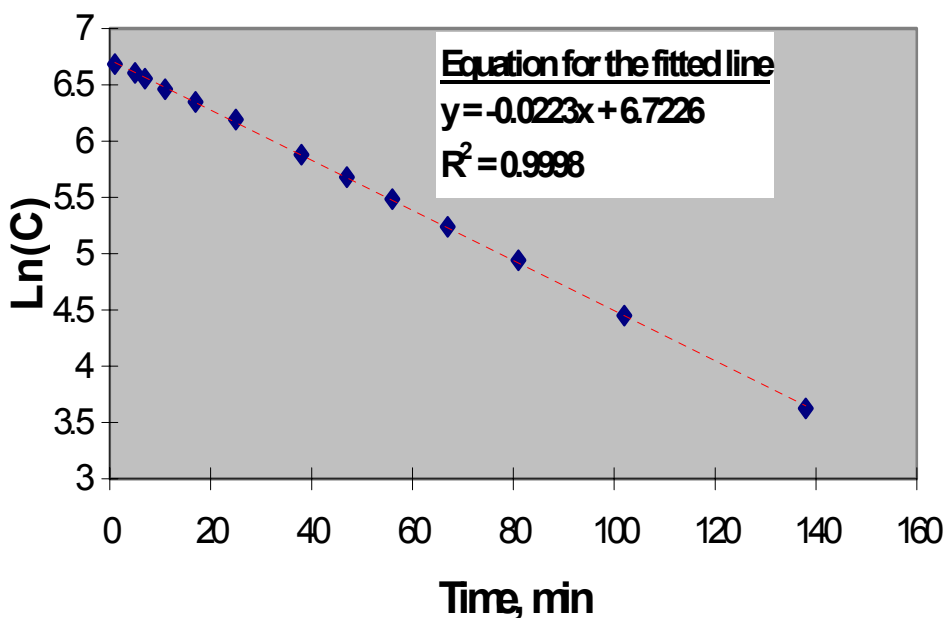
The pump-membrane system was operated in a pervaporation mode, with a gas (nitrogen or air) sweeping on one side of the membrane and MTBE-containing water circulating on the other side. A bench top SeleXtrac™ Lab System (Figure 3-2) and analytical test equipment was made available for in-house testing. The water circulating flow rates were varied to determine the significance of liquid film mass transfer resistance versus the liquid membrane resistance. The gas sweeping flow rate was deliberately set high to minimize gas film resistance. Most of the experiments were made with the water circulating tangentially through the lumens of the fibers, which represents a more precisely defined fluid flow geometry. For comparative purposes, a few experiments were carried out with the water circulating through the shell side of the modules.

In a typical experiment, MTBE concentration in the test solution was monitored as a function of time at a certain circulating flow rate. The results from one experiment are shown in Table 3-3. Figure 3-3 shows the excellent data fit using a simple transport model. The transport rate expressed as the magnitude of the overall mass transfer coefficient,  $K_f$ , for a particular experiment can be calculated from the slope of the fitted line.

**Table 3-3**

**MTBE Removal with Si-350-Coated SeleXtrac™ Module. Feed (lumen): 0.1% MTBE in water circulating at 430 ml/min; Volume = 958.7 ml Strip (shell): nitrogen sweep at 5 L/min**

Time (min)	MTBE in Feed (ppm)
1	799.7
5	739.7
7	703.7
11	638.7
17	571.7
25	487.7
38	357.7
47	292.7
56	240.7
67	188.7
81	139.7
102	85.5
138	37.5
190	11.6



**Figure 3-3**

**MTBE Transport with Si-350-Coated the SeleXtrac™ MiniKros Sampler**

Table 3-4 summarizes all the results obtained for the two modules, one un-coated and one coated, with water through the lumen. It can be seen that the transport rates clearly increased at higher water circulating rates, from about  $4 \times 10^{-4}$  cm/s at 200 ml/min to  $6 \times 10^{-4}$  cm/s at 1000 ml/min. This indicates that the liquid-side mass transfer resistance (as supposed to membrane resistance) is important in this flow regime and needs to be considered during scale up. The transport rates started to level off above 500 ml/min, corresponding to a linear velocity of about 15 cm/s and a Reynolds number of about 80.

**Table 3-4**  
**Results of MTBE removal of a coated vs. an uncoated module**

Shell Side N <sub>2</sub> , L/min	Lumen Side Feed, ml/min	MiniKros Sampler (PS 400K, 680 cm <sup>2</sup> )	
		K <sub>f</sub> , cm/s	
		Silicone Coated	Un-Coated
5	210	3.94E-04	2.6E-04
5	280	4.68E-04	
5	430	5.23E-04	2.6E-04
5	510	5.71E-04	
5	775		2.2E-04
5	1020	6.07E-04	

The un-coated module exhibited lower transport rates ( $2.2\text{--}2.6 \times 10^{-4}$  cm/s) than the coated one. This was unexpected since the presence of the liquid polymer instead of just open pores should retard the transport of MTBE through the membrane, which can occur by volatilization. It was suspected that water vapor might have condensed inside the open pores of the uncoated fibers, effectively creating a water film that MTBE had to diffuse through. In addition, the mass transfer rate was relatively independent of liquid flowrate for the un-coated module. Based on the estimated MTBE diffusivity in water of  $8.67 \times 10^{-6}$  cm<sup>2</sup>/s and the membrane characteristics listed in Table 3-2, the resulting mass transfer coefficient through a water-filled membrane would be  $2.7 \times 10^{-4}$  cm/s, which is reasonably close to the measured values. We also observed a significant amount of moisture collected in the tubing on the gas side during the experiments with the uncoated module only and not with the silicone-coated modules.

Thus the liquid polymer coating results in a double benefit: it forms a physical barrier to ensure separation between the contaminated water on the other side of the membrane and enhances the overall transport rate by preventing possible condensation of water vapor in the membrane pores. The Si-350 coated membrane module was found to be very stable. Tests were conducted for several weeks with no reduction in performance.

We also tested two other modules in which water was circulating on the shell side and gas sweeping through the lumen. At a flow rate of 1000 ml/min, the calculated mass transfer rate ranged from  $5.7$  to  $7.5 \times 10^{-4}$  cm/s, which was comparable to the  $6.1 \times 10^{-4}$  cm/s shown in Table 3-4. For well-engineered designs, such as radial flow or cross flow, the mass transfer rate on the shell side can be higher than in the lumen. However, with the simple shell and tube configuration, the mass transfer rate on the shell side tends to drop significantly upon scale-up due to poor contact between the circulating liquid and the large number of fibers in big modules.

This aspect will need to be carefully considered in the module design for the eventual large-scale operation.

#### **IV. INTEGRITY TESTING OF COATING METHOD**

Integrity testing was conducted using the SeleXtrac™ MiniKros Sampler module coated with Polybutylene Glycol (PBG) using the coating method described in Addendum 2.0. Two coating solutions were used: undiluted PBG and a solution of PBG in isopropyl alcohol. The integrity test involves a gas permeation measurement and a membrane transport measurement for a group of organic compounds through the coated membrane.

##### **1. Gas Permeation Testing Procedure**

All modules were tested using a standard gas permeation method. The procedure involves applying increasing amounts of nitrogen pressure on the lumen side which is controlled with a back pressure regulator, while simultaneously monitoring the gas flow rate on the shell side (extracapillary side) of the membrane. The gas permeation is electronically monitored using a flow or bubble meter. In general, pressures of 5 to 30 psi will yield a linear plot of gas flow rates from about 2ml/min to 1liter/min.

##### **2. Water Soluble Organic Compounds Testing Procedure**

Selected modules were tested as representative samples of the coated groups. The feed mixture of water soluble organics circulated on the shell side, while a strip solution of double distilled water was collected as the permeate on the lumen side. About one liter of each solution was recirculated in a countercurrent mode at 1 l/min. The strip solution was sampled periodically and analyzed for soluble organic compounds via Gas Chromatogram using a Flame Ionization Detector (GC/FID). The transport rates ( $K_p$ ) were calculated for each compound and compared.

Nine PBG-coated modules were tested: four with a mixture of PBG/IPA and five with undiluted PBG. All nine coated modules and one uncoated module (control), were tested using the gas permeation test. The results are shown in Table 3-5. All four of the PBG/IPA coated modules passed the gas permeation test (gas permeation less than 100 cc/min at 5 psi applied pressure). Only two (module # 4B and 8B) actually exhibited a continuous gas barrier (flux below the calculated ~1 cc/min based on gas permeation through the liquid polymer layer). Four of the five modules coated with undiluted PBG failed the permeation test. The high viscosity of the PBG makes the coating process difficult and only the “well loaded” modules with the membrane pores completely filled were acceptable (5B) as shown by no observable gas permeation at test pressures to 30 psi.



**Table 3-5**  
**Results of Integrity Testing for SeleXtrac™ MiniKros Modules**

Monsanto Code	Spectrum lot#	PBG ONLY or PBG/IPA LOADING	PBG Loaded (g)	Passed gas perm test?	Flow @ 5 psi (ml/min)	K <sub>f</sub> Test?
47	13300-8B	PBG/IPA	1.62	Pass	0.5	Yes
48	13300-10B	PBG/IPA	1.84	Pass	60	
49	13300-3B	PBG/IPA	1.97	Pass	15	
50	13300-4B	PBG/IPA	2.39	Pass	0.5	
51	13300-1B	PBG ONLY	2.05	Fail	12926	Yes
52	13300-2B	PBG ONLY	2.11	Fail	19900	
53	13300-6B	PBG ONLY	2.24	Fail	22782	
54	13300-9B	PBG ONLY	2.25	Fail	23682	Yes
55	13300-5B	PBG ONLY	2.77	Yes	0	
		No Coating	0.00	Fail	32500	

Transport rate measurements were conducted for a group of organic compounds using three PBG-coated modules. The general trend shown was similar to earlier observations: the less polymer loading, the faster the transport of the organic compounds. However, during the coating process, if not enough polymer is loaded into the membrane pores to produce a continuous PBG layer, a breakthrough of an organic compounds can be detected when the modules are tested using ethylene glycol as a marker. In addition to the adequate amount of PBG, the distribution of the polymer throughout the pores is critical. These tests also showed that it is advantageous to dilute the polymer with a suitable solvent to obtain a high K<sub>f</sub>. A 50% mixture of PBG/IPA provides a suitable polymer solution to impregnate the pore of the membrane. The slow volatilization of IPA helps to create a thinner, continuous layer. On the other hand, if undiluted PBG is used, the polymer tends to self-aggregate and prevents a uniform layer to form on the surface of the membrane. A thick layer of polymer results in a reduction of transport rates.

## V. CONCLUSIONS FROM PHASE I

During this phase we evaluated two important factors in the development of SeleXtrac™ membranes for removal of MTBE from contaminated water: selection of the liquid polymer and evaluation of a current SeleXtrac™ hollow fiber module. We evaluated polybutylene glycol 4800 (PBG-4800) and Silicone 350 (Si-350), the two most promising polymers for this application based on our previous experience. The test results indicated that the Si-350 membrane system exhibited an MTBE transport rate twice that obtained with PBG-4800. This was most likely a consequence of MTBE diffusing faster through Si-350, which is about 1/3 less viscous than PBG-4800. Both liquid polymers exhibited similar solubility for MTBE, as shown by the measured partition coefficient (K<sub>p</sub> is about 9).

With Si-350 as the preferred liquid polymer, a small bench-scale hollow fiber SeleXtrac™ membrane module (MiniKros Sampler) was used to test the removal of MTBE from water. The membrane system was operated in the pervaporation mode, with gas sweeping on one side of the

membrane and MTBE-containing water circulating on the other side. The overall transport rates increased up to 50% at higher liquid flow rate, suggesting that liquid-side mass transfer resistance could be significant. The non-coated control membrane unit exhibited much lower transport rates (about  $\frac{1}{2}$  to  $\frac{1}{3}$ ) than the Si-350 membrane. It was possible that water moisture could have condensed in the membrane pores of the uncoated module, creating a water film that retarded MTBE transport. Thus, the liquid silicone used in this supported polymeric liquid membrane process appears to have a double benefit: enhancing the transport rate as well as forming an effective physical barrier between the contaminated water and the other side of the membrane.

These tests show that hollow fiber modules can be coated as long as sufficient amount of polymer is used to ensure complete impregnation of the polymer into the pores of the membrane. The PBG/IPA coating approach yields a thinner and more uniform continuous layer of PBG into the pores and on the surface of the hollow fibers. This will insure that the coated modules are integral and will maximize the transport rates of the compounds of interest. The results show that both coating solutions are acceptable. However, care needs to be taken when using undiluted PBG to ensure that the membrane pores are completely filled with the polymer.

Based on the success of these preliminary results, we initiated the second phase of the study using larger conventional tangential flow modules impregnated with Si-350 to establish a baseline against which we could evaluate the performance of the radial dispersion KrosTrac modules.

# 4

## MEMBRANE SUPPORT AND MODULE DESIGN

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With the liquid polymer selected and the basic operating conditions defined, we next evaluated the effects of membrane structure and module design on the system performance, including liquid membrane stability and transport rates. The new information was intended to provide the basis for the development of spinning conditions to create SeleXtrac™ membranes that are optimized for this application. This section presents the development of the manufacturing process of the innovative axial configuration. The various steps are outlined below

### I. SPINNERET DESIGN

A three-channel spinneret was designed to provide control of the spinning process to form a hollow fiber with the proper physical dimensions and pore size. This type of spinneret construction allows accurate metering of the chemical composition through the spinneret nozzle, the coagulating core fluid and the external chemical coating of the membrane surface for optimum hollow fiber structure (Figure 4.1).



**Figure 4-1**  
**3-Chanel Spinneret System**

### II. AXIAL FLOW GEOMETRY MODULE DESIGN AND CONSTRUCTION

Based on prior experience in the design of hollow fiber gas exchange systems and hemodialyzers, we chose an axial winding pattern consisting of sixteen parallel hollow fibers wound around a perforated core. The core (Figure 4-2) provides for two radial dispersion fluid distribution zones whereby the feed fluid is forced to percolate at a high velocity through a mat

of concentric hollow fiber layers in which such concentric layers radially intercept with one another at a 30 degree angle (Figure 4-3). The winding machine is shown in Figure 4-4. The fluid flow direction is such that it perfuses the first half of the module radially outward toward the outside of the fiber bundle and then circulates in the reverse direction toward the center perforated core and out of the module through the outlet port (Figure 4-5). A finished module is shown in Figure 4-6. The purpose of this flow pattern was to minimize the fluid boundary layer on the surface of the membrane vs. tangential flow configuration.



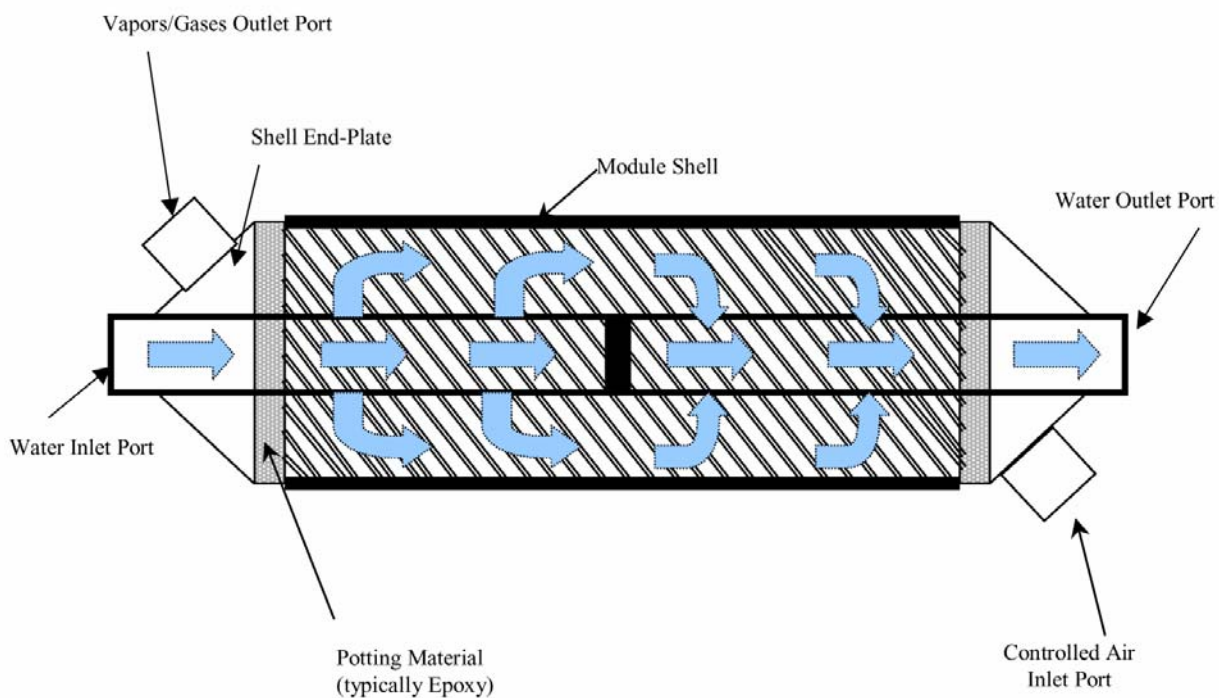
**Figure 4-2**  
**Radial Dispersion Core**



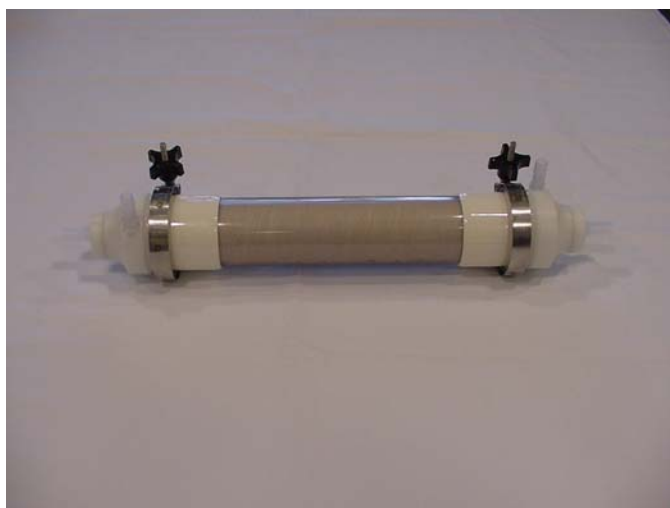
**Figure 4-3**  
**30° Angle Winding Pattern**



**Figure 4-4**  
**Winding Machine**



**Figure 4-5**  
**Basic Fluid Flow in an Axial SeleXtrac™ Module (not to scale)**



**Figure 4-6**  
**SeleXtrac™ Module**

### **III. COATING OF HOLLOW FIBERS**

The formulation of the chemical composition of the solution to be spun into hollow fibers (commonly referred as the DOPE), consisted of 18-20% polymer, 60-70 % solvent, 15-20 % of a pore former and a wetting agent.

### **IV. FABRICATION OF 35 FT<sup>2</sup> MODULES**

Thirty modules of the tangential flow geometry (35 ft<sup>2</sup>) were assembled using the PS hollow fibers described above. These were tested in a larger capacity Pilot Test System that was made available to the University of California, Santa Barbara (UCSB) for their studies, as detailed in the next section.

Thirty axially wound modules (35 ft<sup>2</sup>) were then assembled in three lots of 10 modules. As test results became available from UCSB, the tension on the winding machine (Figure 4-4) was adjusted to add surface area to the modules. Further test results indicated that this method of increasing the surface area of the modules was not successful, since it constrained the flow pattern.

The engineering paper design for an industrial sized module (1500 ft<sup>2</sup>) was postponed indefinitely pending the results of the feasibility study at UCSB. Similarly, the conceptual design of the pumping system for the large industrial scale modules were also postponed.

# 5

## FEASIBILITY STUDY OF MTBE TREATMENT PROCESS

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The objective of this phase of the study was to test the suitability of SeleXtrac™ Liquid Polymer hollow fiber membrane modules for the removal of MTBE, under a number of experimental conditions. If successful, this work is likely to lead to the development of a very innovative treatment system for water contaminated with MTBE or other relatively soluble VOCs. These studies were conducted at Dr. Keller's laboratory in the University of California, Santa Barbara, under contract with Spectrum Laboratories, Inc.

This section covers the experimental studies on two different SeleXtrac™ configurations: 1) tangential flow modules and 2) axial flow modules. In both cases the fibers were Polysulfone (PS) fibers, with a porosity of 400 kD, impregnated with Silicone 350, evaluated under both pressurized sweep gas and vacuum (pervaporation) conditions, at room temperature. In addition to evaluating the performance of the membranes in the removal of MTBE and other VOCs, we determined the overall mass transfer coefficient for each geometry as a function of operating conditions. We used this information to develop preliminary treatment cost estimates, and compare the technology against standard treatment technologies such as air stripping and GAC.

### I. MEMBRANE CONSTRUCTION

The tangential flow membranes used in this study are 351 mm (13.8") long. The module has an overall external diameter of approximately 67 mm (2.6") and an internal diameter of approximately 64 mm (2.5"). Based on the information provided by Spectrum Laboratories, Inc., each module contains 5,414 PS fibers. The external and internal diameters of the fibers are 0.66 and 0.5 mm respectively. The outside membrane surface area is 3.5 m<sup>2</sup>, while the inside surface area is 2.7 m<sup>2</sup>, as reported by Spectrum Laboratories, Inc. The fibers are coated with Si-350 and are arranged along the length of the HFM module. The lumen side ports are at the top and bottom of the module, while the shell side ports are on the sides of the module. The aqueous solution of MTBE or other VOCs flows upward through the module, in the lumen (inside) of the fibers, while the sweep gas flows downward under counter-current conditions, outside the fibers.

The experimental axial flow geometry is achieved by Spectrum using cross-wound hollow fiber membrane modules (KrosTrac™). In this case the fibers are wound on a shaft at approximately a 30° angle. Water enters the module through the inner shaft, passes through some slotted perforations in the shaft, past the outside (shell side) of the membranes and returns through the membranes to the inside of the shaft further downstream, as shown in Figure 8-1. This additional contact between the organic-laden water and the membranes should provide increased mass transfer. Under this configuration, air passes through the inside (lumen side) of the membranes.

As before, the PS 400 kD fibers are impregnated with Silicone 350. Impregnation with the liquid polymer is performed after the winding is completed and the fibers have been potted with epoxy in the membrane module. The aqueous solution of MTBE or other VOCs flows upward through the module, while the sweep gas flows downward under counter-current conditions.

Spectrum provided us with two different KrosTrac™ constructions. The first construction had a looser weaving of the membranes around the central shaft. Initially six membranes (labeled 1-6) were delivered to our laboratory with this first construction. Of these, four presented leakage across the membrane or in the flanges and were returned to Spectrum. A second set of six membranes (labeled I-VI) was constructed and delivered to UCSB for testing. The average internal surface area of this set was 2.48 m<sup>2</sup>, as reported by Spectrum. This second set was constructed to determine the repeatability of the manufacturing process. Collectively these membranes are referred to as the First Construction in this report.

In between the two sets mentioned above, Spectrum constructed two sets of membranes with a tighter weaving. The first set (labeled 7-9) appeared to be unevenly coated with the polymer, possibly due to the tighter weaving. It was not possible to test it due to the leakage of fluids across the membrane. The second set (labeled 10-14) had two membranes with leakage (#12 and 13). The average internal surface area of this set was 4.06 m<sup>2</sup>, as reported by Spectrum. These membranes are referred to as the Second Construction in the report.

The report first briefly presents the theoretical basis for developing a model of mass removal using Liquid Polymer SeleXtrac™ modules, which allows us to scale up to various flow rates and compare with other technologies. We then present the methods and discuss the experimental results. We conclude with the economic analysis and our recommendation for future research and application of these membranes.

## II. THEORY

Transfer of organics from the aqueous phase through the membrane to the gas phase is driven by the concentration gradient. The constant airflow past the membrane effectively keeps the air phase concentration of the contaminant near zero, allowing continuous diffusion of organic molecules from the water to the membrane, through the liquid polymer, which is very hydrophobic, and to the air side. Three resistances limit the contaminant's rate of diffusion through the membrane: Equation 5-1 diffusion through the water to the membrane surface ( $1/k_w$ ), Equation 5-2 diffusion through the pores of the membrane filled with liquid polymer ( $1/k_m$ ), and (Equation 5-3 diffusion from the membrane surface into the bulk air ( $1/k_g$ ). The transfer coefficients through the air-filled pores and the bulk air are expressed in terms of water-phase transport by multiplying by the Henry's constant of the organic,  $H$ . The overall mass transfer coefficient,  $K_{oL}$  (m s<sup>-1</sup>) for the contaminant is the reciprocal of the sum of the individual resistances (Costello, Fane et al. 1993; Castro and Zander 1995):

$$\frac{1}{K_{oL}} = \frac{1}{k_L} + \frac{1}{Hk_M} + \frac{1}{Hk_G}$$

**Equation 5-1**



The aqueous and gas phase mass transfer coefficients depend on operating conditions, especially water ( $u_w$ ) and gas ( $u_g$ ) velocities in  $\text{m s}^{-1}$ , the characteristic length ( $d_e$ , inner diameter of the fiber, m), the kinematic viscosity of the fluids,  $\nu_p$ , in  $\text{m}^2 \text{s}^{-1}$ , and the diffusivity of the organic in either phase,  $D_p$ , in  $\text{m}^2 \text{s}^{-1}$ . The subscript p denotes the liquid or water phase (w or g, respectively). Since the diffusivity of most volatile and semivolatile compounds is approximately four orders of magnitude smaller in water than air (Schwarzenbach, Gschwend et al. 1993), the resistance due to diffusion through the water phase generally controls the overall mass transfer rate.

Removal of VOCs from water can be modeled assuming a plug flow reactor with a constant mass transfer coefficient along the length of the fiber (Aptel and Semmens 1996):

$$-u_w \frac{dC_w}{dx} = K_{oL} A (C_w - C_g^*/H) \quad \text{Equation 5-2}$$

where  $x$  = linear dimension along the length of HFM unit (m),

$A$  = interfacial area of membrane per unit volume in module ( $\text{m}^2 \text{m}^{-3}$ ),

$C_g^*$  = equilibrium concentration of VOC in the gas phase ( $\text{mol L}^{-1}$ ).

As a first approximation, it can be assumed that  $C_g^*$  is negligible given that the airflow tends to remove the molecules relatively fast from the membrane surface and bulk air phase within the membrane. Equation 5-2 can be solved to find the concentration at the outlet,  $C_{w,L}$ :

$$C_{w,L} = C_{w,0} \exp[-K_{oL} A (L / u_w)] \quad \text{Equation 5-3}$$

where  $L$  is the actual length of the fibers.

Based on previous work by Yang and Cussler (1986) and Keller and Bierwagen (2001), the overall mass transfer coefficient can be related to the liquid and gas flowrates using the following relationships:

$$Sh_w = a_1 Re_w^{a_2} Sc_w^{a_3} \quad \text{Equation 5-4}$$

and

$$Sh_g = b_1 Re_g^{b_2} Sc_g^{b_3} \quad \text{Equation 5-5}$$

where the Sherwood ( $Sh_p$ ) =  $\frac{k_p d_e}{D_p}$ , Reynolds ( $Re_p$ ) =  $\frac{u_p d_e}{\nu_p}$  and Schmidt ( $Sc_p$ ) =  $\frac{\nu_p}{D_p}$  numbers are used to characterize the system in non-dimensional form. The empirical coefficients  $a_{1-3}$  and  $b_{1-3}$  are determined experimentally. The values of  $\nu_p$  and  $D_p$  are calculated following (Keller and Bierwagen 2001). Once the parameter values have been determined for this system (liquid polymer HFM with PS fibers impregnated with Si-350), it is possible to predict the removal efficiency for a larger membrane module using Equation 5-3.

### III. EXPERIMENTAL SETUP AND APPROACH

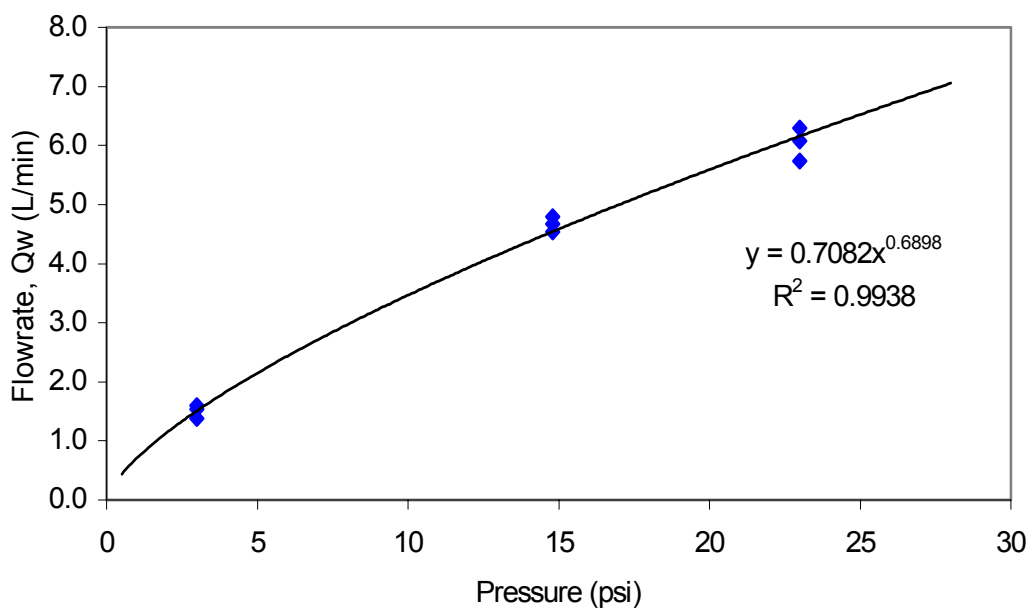
Figure 5-1 depicts the Pilot Scale setup provided by Spectrum Laboratories for testing at UCSB. A schematic of the experimental setup is shown in Figure 5-2. The Spectrum KrosFlo™ Pilot System was used for all experiments. Water spiked with MTBE was held in a 50-L plastic carboy. Typical concentrations of MTBE were in the 1-100 mg/L range, although some studies were conducted at almost 1000 mg/L, and a few were conducted at less than 1 mg/L. An aqueous solution saturated with MTBE or the desired organic was added to the 50-L carboy to produce the desired concentration. The liquid solution was then fed into a Waukesha Cherry-Burrell Pump (Model 018) by gravity. Liquid pressure was measured using an Anderson Instruments pressure gauge (-1.0 to 2.0 bar, 30 in. Hg vacuum to 30 psi), and flow rate was measured at the exit of the membrane using a Cole-Parmer flowmeter (0-9 L/min). The liquid flow rate was also measured independently, to calibrate the flowmeter, and to generate a correlation between the liquid pressure and flowrate (Figures 5-3 and 5-4, for the two types of membranes).



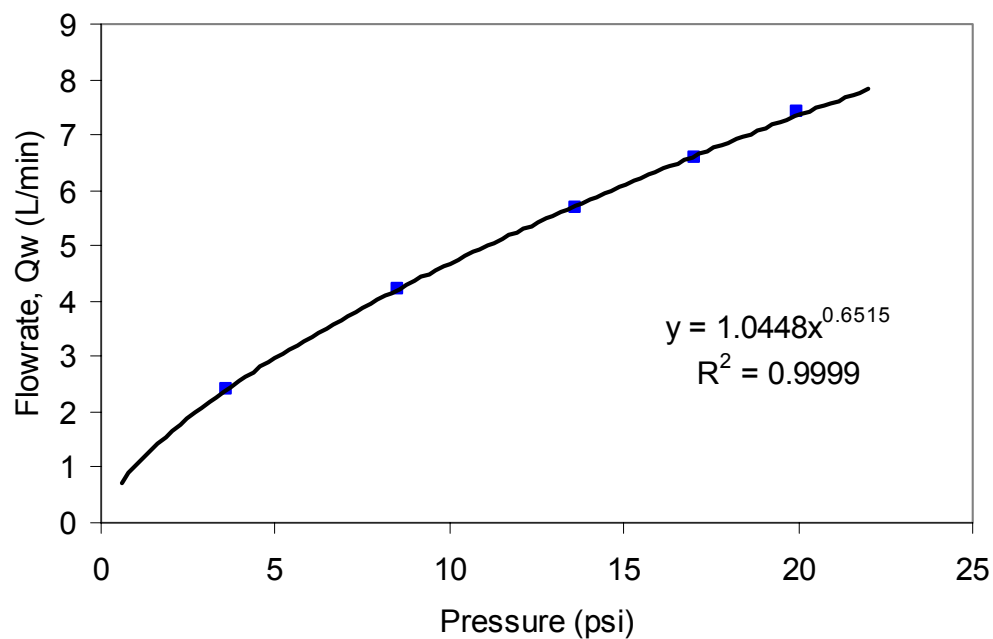
**Figure 5-1**  
**Pilot System**

Air or vacuum pressures were measured using a Gast manometer, while gas flow rate was measured using a Cole Parmer flowmeter (0-4 ft<sup>3</sup>/min). Vacuum pressures of 0.23 and 0.73 atm were tested, with corresponding gas flow rates of 80 (2.8 cfm) and 45 (1.6 cfm) standard L/min. The process was run at constant room temperature, approximately 22 °C, for approximately 60 min. at each set of operating conditions.

**Figure 5-2**  
**Simplified flow diagram**



**Figure 5-3**  
**Flow Rate vs. Pressure for Tangential HFM**



**Figure 5-4**  
**Flowrate vs. Pressure for KrosTrac™ Membranes**

Aqueous samples were collected in 1-mL vials, every 12 minutes, noting the precise time of collection from the start of each run. The samples were analyzed using a Hewlett-Packard Gas Chromatograph/Mass Spectrometer with an auto-sampler, with direct injection of the aqueous solution into the gas chromatograph, following the method developed by Hong, Duttweiler et al. (1999).

The process was run under recycle mode, with the concentration of MTBE decreasing exponentially over time, assuming a first-order mass transfer process:

$$\frac{dC_{MTBE}}{dt} = -\left(\frac{K_{oL}A_m}{V_f}\right)C_{MTBE} \quad \text{Equation 5-6}$$

$C_{MTBE}$  = MTBE concentration in solution, (mg/L)

$t$  = time, (s)

$K_{oL}$  = overall mass transfer coefficient, (m/s)

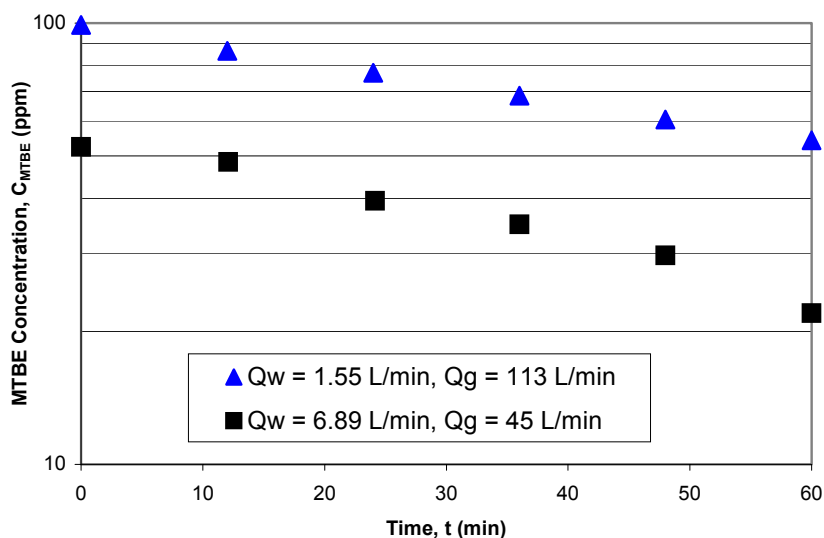
$A_m$  = total membrane area, (m<sup>2</sup>)

$V_f$  = volume of feed solution, (m<sup>3</sup>)

The overall mass transfer coefficient,  $K_{oL}$ , was obtained from the slope of a plot of the natural logarithm of  $C_{MTBE}$  over time.

## IV. EXPERIMENTAL RESULTS

MTBE is readily separated from the aqueous solution using the PS hollow fiber membranes coated with Si-350. Figure 5-5 presents results from two sample runs at different conditions.



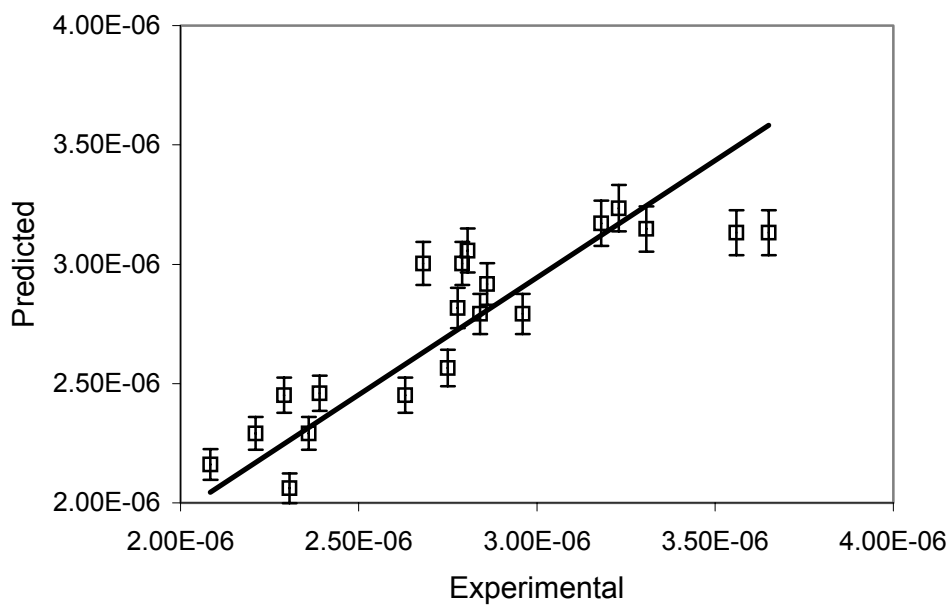
**Figure 5-5**  
**MTBE Removal in Transverse Flow**

The corresponding overall mass transfer coefficients for various operating conditions are presented in the Addendum 1.0. For the traditional construction (tangential flow), a least squares fit of the experimental results to Equations 5-1, 5-4 and 5-5 was performed. Comparisons between the observed and predicted overall mass transfer coefficients for vacuum and pressurized air conditions are presented in Figures 5-6 and 5-7. The comparisons indicate somewhat larger variability in the experimental results than expected. The resulting values for the coefficients  $a_{1-3}$  and  $b_{1-3}$  are presented in Table 5-1 for pressurized air and vacuum conditions. As expected, for the system under study (MTBE in water),  $Sc$  does not vary significantly over the operational range of temperatures ( $\sim 5$  to  $40$  °C), resulting in very small values for  $a_3$  and  $b_3$  (i.e. there is essentially no dependence on  $Sc$ ). It is necessary to perform these experiments with a number of organic pollutants to evaluate the variation due to the molecular diffusivities, which was beyond the scope of the current project.

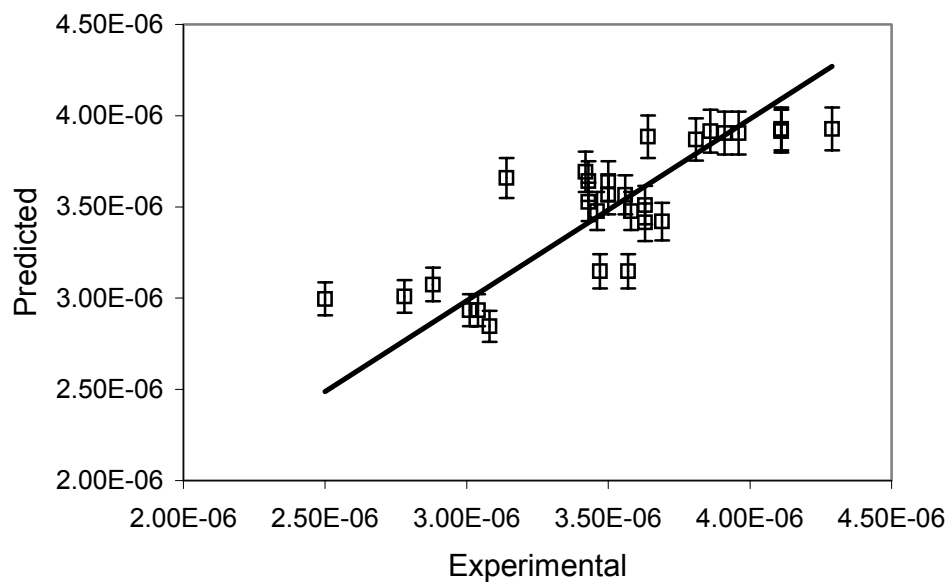
**Table 5-1**  
**Coefficient Values for Mass Transfer Correlations in Tangential Flow**

	Vacuum	Pressurized Air
$a_1$	0.499	0.510
$a_2$	0.213	0.198
$a_3$	0.071	0.108
$b_1$	0.092	0.095
$b_2$	0.497	0.498
$b_3$	0.010	0.010

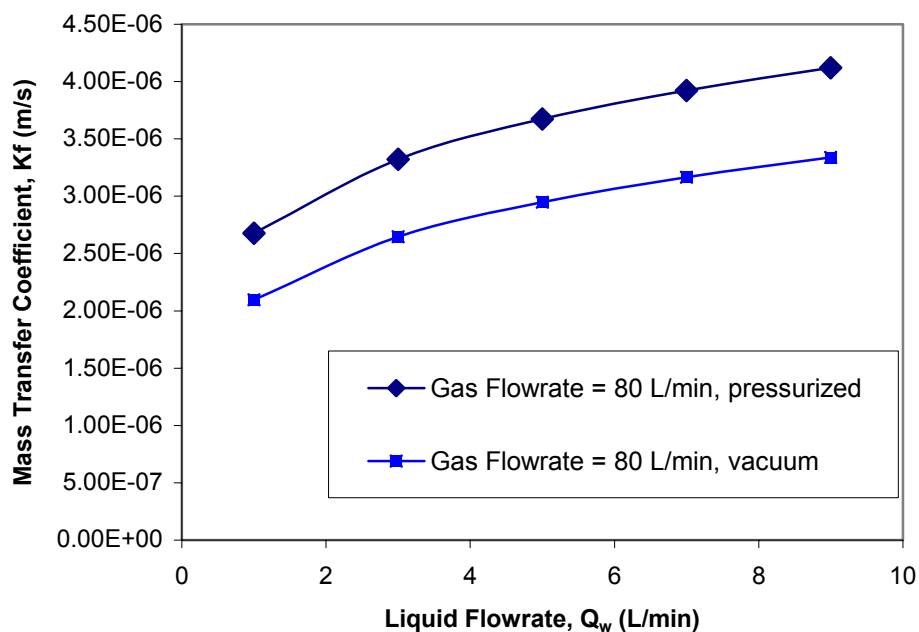
In Figure 5-8 we present a prediction of the overall mass transfer coefficients for tangential flow under vacuum and pressurized air conditions. The model (Equations 5-1, 5-4 and 5-5) predicts negligible dependence on airflow rate. We did not conduct experiments under very low airflow conditions ( $< 40$  L/min), where it is likely that gas flowrate will become a significant factor. There is a clear difference between pressurized air and vacuum conditions, as seen in Figure 8-8. Pressurized air conditions result in approximately 25% greater overall mass transfer coefficient than vacuum conditions, for tangential flow. The model also predicts that the overall mass transfer coefficient is not very sensitive to increasing liquid flowrate. This weak dependence might explain the variability observed in our experiments.



**Figure 5-6**  
**Predicted vs. Experimental Mass Transfer Coefficient (Tangential Flow, vacuum)**



**Figure 5-7**  
**Predicted vs. Experimental Mass Transfer Coefficient (Tangential Flow, pressurized air)**



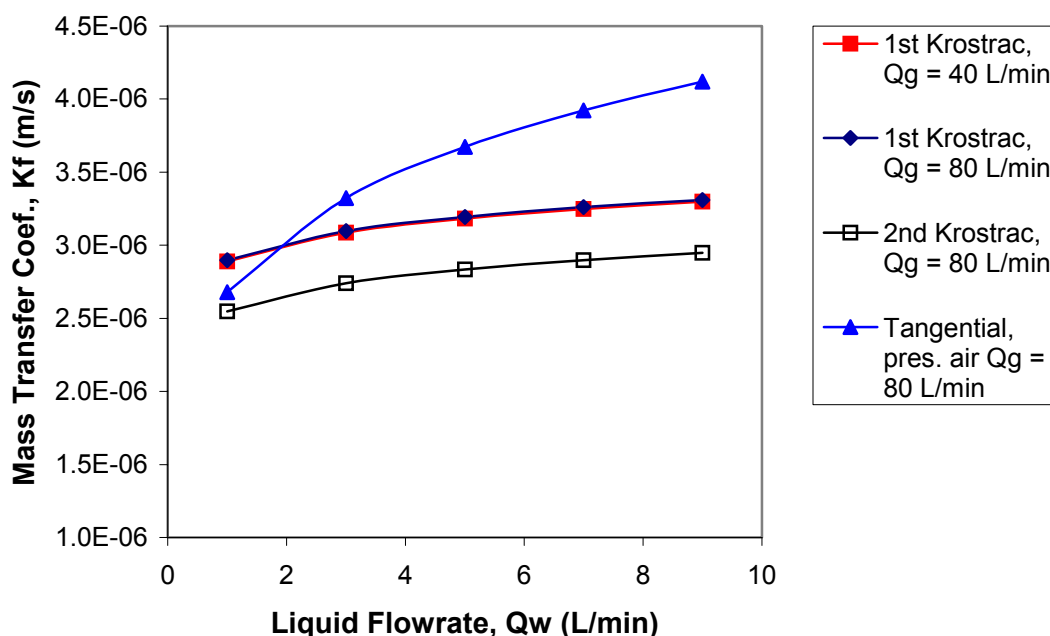
**Figure 5-8**  
**Predicted Overall Mass Transfer Coefficient (Traditional Membrane, transverse flow)**

A similar analysis was conducted for the KrosTrac<sup>TM</sup> membranes. In addition to the manufacturing problems mentioned in the introduction, the KrosTrac<sup>TM</sup> membranes exhibited some variability in their properties (e.g. internal surface area, degree of liquid polymer coating, pressure test results), which was reflected in significant variability in the experimental results. Figure 5-9 presents a comparison of the predicted overall mass transfer coefficient for the three membrane designs: tangential flow (normal construction) and axial flow (KrosTrac<sup>TM</sup>, first and second construction). The corresponding coefficients for the two KrosTrac<sup>TM</sup> construction designs are presented in Table 5-2. The KrosTrac<sup>TM</sup> membranes were also tested under vacuum, but in general the removal of MTBE was very low, so after 15 relatively unsuccessful experimental runs with vacuum conditions, the setup was returned to a pressurized condition.

**Table 5-2**  
**Coefficient Values for Mass Transfer Correlations in Axial Flow**

	1 <sup>st</sup> Construction	2 <sup>nd</sup> Construction
$a_1$	0.550	0.545
$a_2$	0.061	0.067
$a_3$	0.147	0.129
$b_1$	0.095	0.095
$b_2$	0.499	0.499
$b_3$	0.0098	0.0098





**Figure 5-9**  
**Comparison between membrane construction designs**

The traditional construction (tangential flow) had a higher overall mass transfer coefficient at most flowrates than the KrosTrac<sup>TM</sup> membranes. The tighter weaving (2nd KrosTrac<sup>TM</sup> construction) resulted in a reduction in overall mass transfer, negating any benefits from the increased surface area. It is quite possible that the fibers were bound so tightly that the effective surface area for mass transfer was significantly reduced. This might also explain the decreased efficiency of the KrosTrac<sup>TM</sup> relative to the traditional construction. Additional baffling and routing of the water flow might improve the overall contact of water and the membrane. At present, it is likely that a significant fraction of the liquid flow is concentrated in certain regions, thus not using all the available surface area effectively. It should be noted that due to the generally greater surface area of the 2nd construction of KrosTrac<sup>TM</sup> membranes, the removal of MTBE is higher than the 1st construction or the tangential construction.

## V. ECONOMIC ANALYSIS

For the economic analysis, eight different cases were evaluated, generally following Keller, Sandall et al. (2000). These cases are based on a review of data on the typical MTBE concentrations and flow rates required to treat, available from USGS studies (Delzer, Zogorski et al. 1996; Squillace, Zogorski et al. 1996), and (CAL-DHS 2000) information. Concentrations ranging from 100-5,000  $\mu\text{g/L}$  and liquid flowrates in the range of 1-10 gpm are typical of groundwater wells near the source of contamination, usually a leaking underground storage tank. We consider the CAL-DHS secondary MCL level (5  $\mu\text{g/L}$ ) as the treatment goal in our design calculations.

The membrane surface areas required to treat the influent to 5 µg/L are presented in Table 5-3. Considering an average cost of \$75/m<sup>2</sup> of installed membrane area, provided by Spectrum as a typical value, the corresponding cost of the modules was estimated. This membrane cost includes a 40% profit margin, typical of this industry. The estimated life of the membranes is between one and three years, depending on prefiltering and the quality of the influent water, although Spectrum does not have experience with this application of the SeleXtrac<sup>TM</sup> membranes.

**Table 5-3**  
**Membrane area and cost considering treatment to 5 µg/L**

Influent Concentration (µg/L)	100	500	1000	5000	100	500	1000	5000
Liquid Flowrate (L/min)	5	5	5	5	38.75	38.75	38.75	38.75
Surface area KrosTrac 1st (m <sup>2</sup> )	238	365	420	548	1628	2502	2879	3753
Surface area KrosTrac 2nd (m <sup>2</sup> )	267	410	472	616	1814	2789	3208	4183
Surface area Tangential (m <sup>2</sup> )	206	317	365	476	1075	1653	1901	2479
Membrane Cost KrosTrac 1st	\$ 17,820	\$ 27,393	\$ 31,517	\$ 41,090	\$ 122,072	\$ 187,654	\$ 215,899	\$ 281,481
Membrane Cost KrosTrac 2nd	\$ 20,024	\$ 30,781	\$ 35,414	\$ 46,172	\$ 136,055	\$ 209,150	\$ 240,630	\$ 313,725
Membrane Cost Tangential	\$ 15,483	\$ 23,801	\$ 27,383	\$ 35,701	\$ 80,635	\$ 123,955	\$ 142,612	\$ 185,932

If the effluent from the membrane is at 50 µg/l and it is then passed through Granular Activated Carbon, the surface area and cost of the membrane would decrease considerably, as shown in Table 5-4. The cost-effectiveness of this strategy is discussed below.

Since the efficiency of the KrosTrac<sup>TM</sup> membranes is lower than for the traditional tangential construction, the rest of the economic analysis centers on the tangential membranes. In addition to building the membrane modules, the system requires a mounting frame, a water pump, an air blower, piping and instrumentation. The mounting frame and piping costs are scaled based on the total membrane area. Including overhead and margin, the delivered price of the units is presented in Table 5-5. Also included is the estimated annual Operation and Maintenance (O&M) budget, and the estimated cost to treat 1000 gal, a common benchmark in the water treatment industry. Table 5-6 presents the estimates for a system with a GAC unit for polishing the effluent from the Liquid Polymer SeleXtrac<sup>TM</sup> membranes.

**Table 5-4**  
**Membrane area and cost considering treatment to 50 µg/L**

Influent Concentration (µg/L)	100	500	1000	5000	100	500	1000	5000
Liquid Flowrate (L/min)	5	5	5	5	38.75	38.75	38.75	38.75
Surface area KrosTrac 1st (m <sup>2</sup> )	55	183	238	365	377	1251	1628	2502
Surface area KrosTrac 2nd (m <sup>2</sup> )	62	205	267	410	420	1394	1814	2789
Surface area Tangential (m <sup>2</sup> )	48	159	206	317	249	826	1075	1653
Membrane Cost KrosTrac 1st	\$ 4,123	\$ 13,697	\$ 17,820	\$ 27,393	\$ 28,245	\$ 93,827	\$ 122,072	\$ 187,654
Membrane Cost KrosTrac 2nd	\$ 4,633	\$ 15,391	\$ 20,024	\$ 30,781	\$ 31,480	\$ 104,575	\$ 136,055	\$ 209,150
Membrane Cost Tangential	\$ 3,582	\$ 11,900	\$ 15,483	\$ 23,801	\$ 18,657	\$ 61,977	\$ 80,635	\$ 123,955

Capital costs were amortized over a 20-year horizon, at a 4% discount rate, as is typically done in the environmental field. The analysis will produce different results if it is based on a 5-year payback scheme. Since the membranes are expected to be replaced every two years on average, these were not included in the amortization schedule, but rather they are part of the expensed out O&M. Operation and Maintenance (O&M) costs include the cost of replacing the membranes plus a periodic maintenance of the units, materials and electrical power. The costs estimated here are at the feasibility level (accuracy of -30% to +50%). Additional costs, not considered, may be required for pretreatment depending on influent conditions, and effluent or influent storage. O&M costs are calculated based on electrical power requirements (at \$0.12/kW-h), labor (at \$20/hr), parts and materials considering 5% of equipment per year, without the membranes.

For comparison purposes, the cost of treatment using GAC only or air stripping are presented in Tables 5-7 and 5-8 respectively. At these flow rates, GAC is the most cost competitive technology and given its simple operation is the preferred alternative. Air stripping units have been installed in operations where the flow rates are much higher, given the considerable economies of scale. An analysis using the economic model indicated that in order for the membrane systems to be cost-competitive with GAC, the surface area (or unit cost) would have to decrease by a factor of 15-20, or the expected life of the membranes would have to exceed 20 years, reducing considerably the replacement cost. Naturally, a combination of these factors (more efficient mass transfer, lower unit cost and longer life) would also result in a more competitive process.

## **VI. ENERGY EFFICIENCY CONSIDERATIONS**

Although the energy consumption of the various technologies we evaluated is not very significant, it is nevertheless important to evaluate the most energy efficient system. As presented in Tables 5-5 through 5-8, the GAC system would require the least energy, mostly to pump the contaminated water through the bed of activated carbon. This is followed by air stripping, which considers both the pumping of water to the top of the column and the air blower used to bubble in air for the VOC stripping process. The membrane systems would be slightly above air stripping, mainly due to the significant membrane area required to perform the separation of MTBE from water using the SeleXtrac<sup>TM</sup> systems. The energy consumption of these systems is likely to decrease as more efficient membrane designs are developed.

## **VII. CONCLUSIONS**

The results indicate that MTBE can be readily removed from the solution using these membranes.  $K_{oL}$  is a function of liquid flow rate, and almost independent of gas flow rate under the conditions tested. In general,  $K_{oL}$  for the tangential flow membranes was 25% higher than for the axial flow membranes, possibly due to the current flow pattern, which might not result in effective use of the entire membrane surface area. Given the relatively short expected life of the membranes (one to three years), the overall cost of treating water contaminated with MTBE using LP-HFM is currently estimated to be 6-10 times higher than other treatment processes such as granular activated carbon (GAC) or air stripping. Even if the membranes were used in combination with a GAC polishing step, the overall cost of treatment would be 4-8 times higher than GAC alone.  $K_{oL}$  would have to increase by a factor of 15-20 to result in a cost competitive process. Alternatively, the life of the membrane would have to increase to more than 20 years to result in a cost competitive process.

Further research is warranted to determine whether these barriers can be overcome. Specific research issues to address are:

1. Improving the flow of water through the KrosTrac<sup>TM</sup> membranes to make full use of the membrane surface area, which will significantly improve overall MTBE mass transfer to the gas phase;
2. Develop a less expensive membrane;
3. Determine the life expectancy of the membranes under accelerated test conditions.

### ***Acknowledgments***

Dr. Keller acknowledges the contributions of Mina Mitani, Mike Del Toro, Duygu Tokut, Sanya Sirivithayapakorn, Monica Hood and Farah Shamszadeh, who conducted most of the experimental work under his guidance. Dr. Keller also thanks Mr. Jesus Martinez for all the fruitful discussions with regards to membrane construction and operation.

**Table 5-5**  
**Estimated Capital and O&M Costs considering a LP-HFM system only**

Influent Concentration (µg/L)	100	500	1000	5000	100	500	1000	5000
Liquid Flowrate (L/min)	5	5	5	5	38.75	38.75	38.75	38.75
Capital Cost								
Tang. LP-HFM Membrane Cost	\$ 15,483	\$ 23,801	\$ 27,383	\$ 35,701	\$ 80,635	\$ 123,955	\$ 142,612	\$ 185,932
Pump, Blower, Frame, Pipe, Inst.	6,269	8,294	9,166	11,191	22,129	32,674	37,216	47,761
Labor (at \$20/hr)	610	776	848	1,014	2,213	3,079	3,452	4,319
Fabrication cost	22,361	32,871	37,397	47,906	104,976	159,708	183,280	238,012
Overhead (30%)	6,708	9,861	11,219	14,372	31,493	47,912	54,984	71,404
Margin (15%)	<u>4,360</u>	<u>6,410</u>	<u>7,292</u>	<u>9,342</u>	<u>20,470</u>	<u>31,143</u>	<u>35,740</u>	<u>46,412</u>
Estimated Price	\$ 33,430	\$ 49,142	\$ 55,908	\$ 71,619	\$ 156,939	\$ 238,764	\$ 274,004	\$ 355,828
Annualized Capital Cost	\$ 2,934	\$ 4,143	\$ 4,664	\$ 5,873	\$ 12,476	\$ 18,771	\$ 21,483	\$ 27,778
Annual Operating Costs								
Membrane Replacement	\$ 7,741	\$ 11,900	\$ 13,692	\$ 17,851	\$ 40,317	\$ 61,977	\$ 71,306	\$ 92,966
Other spare parts	313	415	458	560	1,106	1,634	1,861	2,388
Labor (at \$20/hr)	555	638	674	757	1,356	1,790	1,976	2,409
Electric Power (at \$0.12/kW-hr)	315	315	315	315	1,261	1,261	1,261	1,261
Total Direct O&M	8,925	13,268	15,139	19,483	44,041	66,662	76,404	99,025
Overhead (30%)	2,678	3,981	4,542	5,845	13,212	19,999	22,921	29,708
Margin (15%)	<u>1,740</u>	<u>2,587</u>	<u>2,952</u>	<u>3,799</u>	<u>8,588</u>	<u>12,999</u>	<u>14,899</u>	<u>19,310</u>
Annual O&M	\$ 13,343	\$ 19,836	\$ 22,633	\$ 29,126	\$ 65,842	\$ 99,660	\$ 114,225	\$ 148,042
Total annual cost LP-HFM	\$ 16,277	\$ 23,980	\$ 27,297	\$ 34,999	\$ 78,318	\$ 118,431	\$ 135,707	\$ 175,820
Volume of water treated (m <sup>3</sup> )	2,497	2,497	2,497	2,497	19,350	19,350	19,350	19,350
Unit cost (\$/m <sup>3</sup> )	<b>\$6.52</b>	<b>\$9.60</b>	<b>\$10.93</b>	<b>\$14.02</b>	<b>\$4.05</b>	<b>\$6.12</b>	<b>\$7.01</b>	<b>\$9.09</b>
Unit cost (\$/1000 gal)	<b>\$ 24.68</b>	<b>\$ 36.35</b>	<b>\$ 41.38</b>	<b>\$ 53.06</b>	<b>\$ 15.32</b>	<b>\$ 23.17</b>	<b>\$ 26.55</b>	<b>\$ 34.39</b>

**Table 5-6**  
**Estimated Capital and O&M Costs considering LP-HFM with a GAC unit for polishing effluent**

Influent Concentration (µg/L)	100	500	1000	5000	100	500	1000	5000
Liquid Flow Rate (L/min)	5	5	5	5	38.75	38.75	38.75	38.75
<b>Capital Cost</b>								
Tang. LP-HFM Membrane Cost	\$ 3,582	\$ 11,900	\$ 15,483	\$ 23,801	\$ 18,657	\$ 61,977	\$ 80,635	\$ 123,955
Pump, Blower, Frame, Pipe, Inst.	3,372	5,397	6,269	8,294	7,042	17,587	22,129	32,674
Labor (at \$20/hr)	472	638	710	876	1,073	1,940	2,313	3,179
Fabrication cost	7,426	17,935	22,461	32,971	26,772	81,504	105,076	159,808
Overhead (30%)	2,228	5,381	6,738	9,891	8,032	24,451	31,523	47,942
Margin (15%)	<u>1,448</u>	<u>3,497</u>	<u>4,380</u>	<u>6,429</u>	<u>5,221</u>	<u>15,893</u>	<u>20,490</u>	<u>31,163</u>
Estimated Price	\$ 11,102	\$ 26,813	\$ 33,580	\$ 49,291	\$ 40,024	\$ 121,849	\$ 157,088	\$ 238,913
Annualized Capital Cost	\$ 1,229	\$ 2,438	\$ 2,959	\$ 4,168	\$ 3,493	\$ 9,789	\$ 12,500	\$ 18,796
<b>Annual Operating Costs</b>								
Membrane Replacement	\$ 1,791	\$ 5,950	\$ 7,741	\$ 11,900	\$ 9,329	\$ 30,989	\$ 40,317	\$ 61,977
Other spare parts	169	270	313	415	352	879	1,106	1,634
Labor (at \$20/hr)	486	569	605	688	637	1,070	1,256	1,690
Electric Power @ \$0.12/kW-hr	315	315	315	315	1,261	1,261	1,261	1,261
Total Direct O&M	2,761	7,104	8,975	13,318	11,579	34,199	43,941	66,562
Overhead (30%)	828	2,131	2,693	3,996	3,474	10,260	13,182	19,969
Margin (15%)	<u>538</u>	<u>1,385</u>	<u>1,750</u>	<u>2,597</u>	<u>2,258</u>	<u>6,669</u>	<u>8,569</u>	<u>12,980</u>
Annual O&M	\$ 4,128	\$ 10,621	\$ 13,418	\$ 19,911	\$ 17,310	\$ 51,128	\$ 65,693	\$ 99,510
Annual GAC cost <sup>1</sup> (capital + O&M)	\$2,378	\$2,378	\$2,378	\$2,378	\$ 10,220	\$ 10,220	\$ 10,220	\$ 10,220
Total annual cost LP-HFM + GAC	\$ 7,735	\$ 15,438	\$ 18,755	\$ 26,457	\$ 31,024	\$ 71,137	\$ 88,413	\$ 128,526
Volume of water treated (m <sup>3</sup> )	2,497	2,497	2,497	2,497	19,350	19,350	19,350	19,350
<b>Unit cost (\$/m<sup>3</sup>)</b>	<b>\$3.10</b>	<b>\$6.18</b>	<b>\$7.51</b>	<b>\$10.60</b>	<b>\$1.60</b>	<b>\$3.68</b>	<b>\$4.57</b>	<b>\$6.64</b>
<b>Unit cost (\$/1000 gal)</b>	<b>\$ 11.73</b>	<b>\$ 23.40</b>	<b>\$ 28.43</b>	<b>\$ 40.11</b>	<b>\$ 6.07</b>	<b>\$ 13.92</b>	<b>\$ 17.30</b>	<b>\$ 25.14</b>

<sup>1</sup>see Table 7 for details

**Table 5-7**  
**Estimated Capital and O&M Costs for comparable GAC units**

Influent Concentration (µg/L)	50	50	100	500	1000	5000	100	500	1000	5000
Liquid Flow Rate (L/min)	5	38.75	5	5	5	5	38.75	38.75	38.75	38.75
Size of Vessel (lb-rating)	250	500	250	250	250	500	500	500	500	1000
Number of Vessels	1	1	2	2	2	2	2	2	2	2
kg GAC/yr	75	565	100	196	263	517	756	1487	1989	3911
Number of GAC replacements/yr	0.7	2.5	0.4	0.9	1.2	1.1	1.7	3.3	4.4	4.3
EBCT <sup>1</sup> (min)	52	14	52	52	52	104	14	14	14	27
Annualized Capital Cost	\$ 490	\$ 1,144	\$ 981	\$ 981	\$ 981	\$ 2,289	\$ 2,289	\$ 2,289	\$ 2,289	\$ 5,359
Annual Operating Costs										
GAC replacement	\$ 276	\$ 2,086	\$ 369	\$ 725	\$ 970	\$ 1,907	\$ 2,791	\$ 5,487	\$ 7,342	\$ 14,434
Labor (at \$20/hr)	\$ 921	\$ 3,487	\$ 616	\$ 1,211	\$ 1,621	\$ 1,593	\$ 2,332	\$ 4,585	\$ 6,135	\$ 6,030
Electric Power (at \$0.12/kW-hr)	\$ 66	\$ 498	\$ 66	\$ 66	\$ 66	\$ 66	\$ 498	\$ 498	\$ 498	\$ 498
Base O&M Cost	\$1,263	\$6,071	1,051	2,002	2,656	3,566	5,622	10,571	13,975	20,962
Overhead (30%)	\$379	\$1,821	\$315	\$601	\$797	\$1,070	\$1,687	\$3,171	\$4,193	\$6,289
Margin (15%)	\$246	\$1,184	\$205	\$390	\$518	\$695	\$1,096	\$2,061	\$2,725	\$4,088
Total O&M Cost	\$1,888	\$9,076	\$1,571	\$2,993	\$3,971	\$5,331	\$8,405	\$15,804	\$20,893	\$31,338
Total annual cost LP-HFM	\$2,378	\$10,220	2,032	2,983	3,637	5,855	7,911	12,860	16,264	26,321
Volume of water treated (m <sup>3</sup> )	2,497	19,350	2,497	2,497	2,497	2,497	19,350	19,350	19,350	19,350
Unit cost (\$/m <sup>3</sup> )	\$0.95	\$0.53	\$0.81	\$1.19	\$1.46	\$2.35	\$0.41	\$0.67	\$0.84	\$1.36
Unit cost (\$/1000 gal)	\$3.61	\$2.00	\$3.08	\$4.52	\$5.51	\$8.88	\$1.55	\$2.52	\$3.18	\$5.15

<sup>1</sup>Empty Bed Contact Time = measure of time of contact between contaminant and activated carbon.

**Table 5-8**  
**Estimated Capital and O&M Costs for comparable Air Stripping units**

Influent Concentration (µg/L)	100	500	1000	5000	100	500	1000	5000
Liquid Flow Rate (L/min)	5	5	5	5	38.75	38.75	38.75	38.75
<b>Capital Cost</b>								
Packed Tower & Pumps	\$ 38,334	\$ 39,560	\$ 40,107	\$ 41,400	\$ 42,963	\$ 46,153	\$ 47,539	\$ 50,763
Instrumentation, Controls, Install.	\$ 42,168	\$ 43,516	\$ 44,118	\$ 45,540	\$ 47,259	\$ 50,768	\$ 52,292	\$ 55,839
Annualized Capital Cost	\$ 5,923	\$ 6,113	\$ 6,197	\$ 6,397	\$ 6,639	\$ 7,131	\$ 7,346	\$ 7,844
<b>Annual Operating Costs</b>								
Parts & Supplies	\$ 2,417	\$ 2,478	\$ 2,505	\$ 2,570	\$ 3,148	\$ 3,308	\$ 3,377	\$ 3,538
Labor (at \$20/hr)	\$ 2,271	\$ 2,339	\$ 2,369	\$ 2,439	\$ 3,276	\$ 3,386	\$ 3,434	\$ 3,545
Electric Power @ \$0.12/kW-hr	<u>\$ 263</u>	<u>\$ 265</u>	<u>\$ 266</u>	<u>\$ 267</u>	<u>\$ 1,995</u>	<u>\$ 2,012</u>	<u>\$ 2,019</u>	<u>\$ 2,037</u>
Total Direct O&M	\$ 4,951	\$ 5,082	\$ 5,140	\$ 5,277	\$ 8,419	\$ 8,706	\$ 8,830	\$ 9,120
Overhead (30%)	1,485	1,525	1,542	1,583	2,526	2,612	2,649	2,736
Margin (15%)	<u>965</u>	<u>991</u>	<u>1,002</u>	<u>1,029</u>	<u>1,642</u>	<u>1,698</u>	<u>1,722</u>	<u>1,778</u>
Total O&M Cost	7,402	7,598	7,685	7,889	12,587	13,015	13,202	13,635
Total Annual Cost Air Stripping	\$ 13,325	\$ 13,710	\$ 13,882	\$ 14,286	\$ 19,225	\$ 20,147	\$ 20,547	\$ 21,478
Volume of water treated (m <sup>3</sup> )	2,497	2,497	2,497	2,497	19,350	19,350	19,350	19,350
Unit cost (\$/m <sup>3</sup> )	\$5.07	\$5.22	\$5.28	\$5.44	\$0.97	\$1.01	\$1.03	\$1.08
Unit cost (\$/1000 gal)	\$ 19.19	\$ 19.75	\$ 19.99	\$ 20.58	\$ 3.66	\$ 3.83	\$ 3.91	\$ 4.09



# 6

## GLOSSARY OF TERMS

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Advanced oxidation processes: a number of processes used to oxidize chemicals using strong oxidizers, generally well below the combustion temperature

Air stripping: bubbling of air in a closed vessel to remove volatile chemicals from the water

Axial flow: flow of water perpendicular to the length of the fibers

Biodegradability: ability to degrade due to the action of biological agents (e.g. microbes)

Bioremediation: treatment of soil or water using biological agents

Concentration gradient: difference in concentration from one location to another

Granular Activated Carbon: a form of carbon that has been treated to generate a high surface area, with many sites for adsorbing chemicals

Henry's constant: ratio of air to water concentrations of a chemical at equilibrium

Hollow fiber: a fiber that has a tubular configuration

Hydrophilic: water-loving chemical

Hydrophobic: water-hating chemical

Laminar flow: slow fluid flow that generates no turbulence

Liquid Polymer: a polymer solution that can flow

Lumen: inside of the fiber

Mass transfer coefficient: a variable that measures the rate at which mass is transferred from one phase to another

Membrane: a thin film of material that separates either two phases (e.g. liquid and gas) or can maintain a concentration gradient across the film

Microporous: with microscopic pores

Pervaporation: evaporation assisted by vacuum pressure

Reynolds number: a dimensionless ratio of advective to viscous processes that is used to determine when flow is laminar or turbulent

Schmidt number: a dimensionless ratio of viscous to diffusive processes

Sherwood number: a dimensionless ratio of mass transfer to diffusive processes

Sorption: the process of binding a chemical to a surface or fluid, physically or chemically

Tangential flow: water flow along the length of the fibers

Volatile Organic Compound (VOC): organic compound with a high tendency to be in the gas phase.

## **NOMENCLATURE**

$A$  = interfacial area of membrane per unit volume in module,  $\text{m}^2 \text{m}^{-3}$

$A_m$  = membrane area,  $\text{m}^2$

$C_g^*$  = equilibrium concentration of VOC in the gas phase,  $\text{mol L}^{-1}$

$C_{MTBE}$  = MTBE concentration in solution,  $\text{mg L}^{-1}$

$C_{w,L}$  = concentration in the water at the outlet,  $\text{mg L}^{-1}$

$d_e$  = inner diameter of the fiber,  $\text{m}$

$D_p$  = diffusivity of the organic in either phase,  $\text{m}^2 \text{s}^{-1}$

$H$  = Henry's constant, (dimensionless)

$k_g$  = gas side mass transfer coefficient,  $\text{m s}^{-1}$

$k_m$  = membrane mass transfer coefficient,  $\text{m s}^{-1}$

$K_{oL}$  = overall mass transfer coefficient,  $\text{m s}^{-1}$

$K_{oL}$  = overall mass transfer coefficient,  $\text{m s}^{-1}$

$k_w$  = water side mass transfer coefficient,  $\text{m s}^{-1}$

$t$  = time,  $\text{s}$

$u_G$  = gas velocity,  $\text{m s}^{-1}$

$u_w$  = water velocity,  $\text{m s}^{-1}$

$V_f$  = volume of feed solution,  $\text{m}^3$

$\nu_p$  = kinematic viscosity of the fluid,  $\text{m}^2 \text{s}^{-1}$

$x$  = linear dimension along the length of HFM unit, m



# 7

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# A

## ADDENDUM

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### ADDENDUM 1.0. EXPERIMENTAL RESULTS FROM FEASIBILITY STUDY

Table A-1  
Mass Transfer Coefficients for Tangential Design Membranes using pressurized air

$Q_g$ L/min	$Q_w$ L/min	$K_{oL}$ m/s
44	4.38	3.56E-06
44	4.87	3.50E-06
44	4.87	3.43E-06
45	6.65	3.81E-06
62	2.29	3.47E-06
62	2.29	3.57E-06
59	1.60	3.04E-06
59	1.60	3.01E-06
60	3.81	3.58E-06
60	3.81	3.46E-06
59	3.48	3.63E-06
59	7.00	4.11E-06
59	7.00	3.86E-06
60	7.10	4.11E-06
60	7.10	4.29E-06
60	1.4	3.08E-06
60	3.5	3.69E-06
60	4.0	3.63E-06
60	4.1	3.43E-06
60	6.9	3.96E-06
60	6.9	3.91E-06
113	1.76	2.50E-06
113	1.8	2.78E-06
113	4.87	3.14E-06
113	5.1	3.42E-06
113	6.61	3.64E-06

**Table A-2**  
**Mass Transfer Coefficients for Tangential Design Membranes using vacuum conditions**

<b>P<sub>vac</sub></b> <b>atm</b>	<b>Q<sub>g</sub></b> <b>L/min</b>	<b>Q<sub>w</sub></b> <b>L/min</b>	<b>K<sub>oL</sub></b> <b>m/s</b>
0.73	45	0.9	2.31E-06
0.73	45	1.2	2.08E-06
0.73	45	2.6	2.75E-06
0.73	45	4.1	2.78E-06
0.73	45	6.01	2.81E-06
0.73	45	6.9	3.31E-06
0.73	45	7.2	3.18E-06
0.73	45	7.85	3.23E-06
0.23	82	1.52	2.21E-06
0.23	82	1.52	2.36E-06
0.23	82	2.09	2.29E-06
0.23	82	2.09	2.63E-06
0.22	82	2.12	2.39E-06
0.23	82	3.86	2.96E-06
0.23	82	3.86	2.84E-06
0.22	82	4.75	2.86E-06
0.23	82	5.45	2.79E-06
0.23	82	5.45	2.68E-06
0.23	82	6.65	3.56E-06
0.23	82	6.65	3.65E-06



**Table A-3**  
**Mass Transfer Coefficients for KrosTrac First Construction Membranes using pressurized air**

$Q_g$ L/min	$Q_w$ L/min	$K_{oL}$ m/s
45.0	1.10	2.80E-06
45.0	1.40	3.26E-06
45.0	1.25	3.03E-06
39.4	1.60	3.51E-06
45.0	1.80	2.76E-06
42.2	1.80	3.38E-06
64.7	1.80	2.88E-06
47.8	1.75	3.13E-06
45.0	2.10	3.03E-06
39.4	2.20	3.25E-06
39.4	2.20	3.31E-06
28.1	2.30	3.13E-06
28.1	2.30	3.21E-06
39.4	2.20	3.19E-06
56.3	2.50	3.40E-06
66.1	2.50	3.14E-06
59.1	2.60	3.04E-06
61.9	2.60	3.83E-06
59.1	2.60	3.46E-06
67.5	2.60	3.25E-06
67.5	2.60	2.79E-06
61.9	2.70	2.52E-06
67.5	2.60	3.15E-06
63.0	2.59	3.18E-06
45.0	4.00	3.16E-06
56.3	4.00	3.50E-06
56.3	4.20	3.16E-06
56.3	4.00	3.50E-06
53.4	4.10	2.80E-06
61.9	4.10	3.07E-06
56.3	4.10	3.47E-06
61.9	4.10	4.31E-06
53.4	4.30	3.24E-06
64.7	4.30	3.17E-06
53.4	4.40	3.57E-06
56.3	4.28	3.36E-06
33.8	5.80	3.67E-06
33.8	5.80	3.48E-06
36.6	6.00	4.17E-06
39.4	6.00	3.18E-06
61.9	6.00	4.04E-06
36.6	6.00	3.56E-06
39.4	6.00	2.15E-06
50.6	6.20	3.18E-06
42.2	6.20	3.18E-06
50.6	6.20	3.07E-06
33.8	6.30	3.54E-06
41.7	6.05	3.38E-06

**Table A-4**  
**Mass Transfer Coefficients for KrosTrac Second Construction Membranes using**  
**pressurized air**

$Q_g$ L/min	$Q_w$ L/min	$K_{oL}$ m/s
78.8	0.90	3.10E-06
45.0	1.10	3.52E-06
42.2	1.10	3.04E-06
73.1	1.60	2.74E-06
53.4	1.27	3.10E-06
45.0	2.10	3.15E-06
45.0	2.20	3.69E-06
56.3	2.20	3.03E-06
67.5	2.20	2.97E-06
28.1	2.20	3.59E-06
47.8	2.20	3.13E-06
45.0	2.30	3.14E-06
45.0	2.30	3.37E-06
84.4	2.50	3.00E-06
67.5	2.50	3.09E-06
25.3	2.50	3.13E-06
87.2	2.60	3.13E-06
90.0	2.60	2.89E-06
56.3	2.60	2.83E-06
56.5	2.36	3.15E-06
45.0	3.80	2.96E-06
90.0	3.80	3.25E-06
39.4	3.80	2.69E-06
67.5	3.80	3.88E-06
45.0	3.90	2.97E-06
87.2	3.90	2.95E-06
39.4	3.90	2.33E-06
63.6	3.90	3.14E-06
47.8	4.00	3.16E-06
90.0	4.10	4.33E-06
56.3	4.10	3.16E-06
61.0	3.91	3.17E-06
39.4	5.80	3.51E-06
54.0	5.80	3.33E-06
43.6	5.90	3.18E-06
84.4	6.00	3.10E-06
81.6	6.00	3.52E-06
30.9	6.00	2.96E-06
42.2	6.00	3.18E-06
87.2	6.10	2.92E-06
25.3	6.10	2.86E-06
45.0	6.50	2.89E-06
56.3	6.70	3.71E-06

## ADDENDUM 2.0: SI-350 POLYMER LOADING PROCEDURE

The purpose of this procedure is to fill the membrane pores with liquid polymer.

### Equipment Required:

1) Low pressure peristaltic pumps

2) Electric Stirrer (Optional)

3) Rubber bulb pressure tester

4) Fixtures:

### Material:

1) 570-10944-002 Food grade Dow Corning 200 Fluid Silicone (dimethylpolysiloxane, CST=350)

2) IPA (isopropyl alcohol)

3) Modules that have passed the pressure test

Clamps: Use to hold module vertically

Manifold: Use to purge the excess liquid polymer.

Procedure to calculate the amount of liquid polymer required per module.

The formula for calculating the required volume of liquid polymer is:

$$\text{Pore-Volume} = (\text{OD}^2 - \text{ID}^2) * \pi / 4 * L * N * \text{Porosity}$$

Where: OD is the outside diameter of the hollow fiber

ID is the inside diameter of the hollow fiber

L is the fiber length

N is the number of fibers in one module

Porosity is approximately 40% for 400 KD PS (Polysulfone) fiber

The amount of liquid polymer in the pores should be equal to or up to 50% larger than the pore volume.

For example, OD=0.066 cm., ID=0.050 cm, L=12 cm, N= 270, Porosity=0.40. Pore-volume will be 1.89 cm<sup>3</sup>. Therefore, the amount of liquid polymer in the pores should be in a range of 1.89 g to 2.84 g.

## PROCEDURE FOR LOADING THE KrosTrac™ MEMBRANE MODULE WITH POLYMER.

### 1.0 Liquid polymer Preparation:

- 1.1 Silicone liquid polymer is a low viscosity liquid. In order to fill the membrane pores completely, a mixture of 2:1 by volume Silicone/IPA ( $\pm 2\%$ ) is needed.(2 parts Silicone: 1 part IPA).

### 2.0 Procedure to infuse the liquid polymer into the membrane pores:

**NOTE:** Before performing this procedure, two preparatory steps are required: The modules have to pass the integrity leak test. The information label needs to be placed on the module housing approximately in the middle.

- 2.1 Set up module system for flow circulation. Connect 1 ½” sanitary outlet with ¼” hose barb to a KrosFlo end cap using a sanitary clamp.
- 2.2 Attach a 12-inch long flexible tubing to the above port with ¼” barb connector.
- 2.3 Connect the assembled components from step 20.1 – 20.2 to one end of the module.
- 2.4 Repeat step 20.1-20.3 for the other end of the module.
- 2.5 Secure the module in a vertical position using the appropriate clamp. The end of the tubing connected to lower end of the module is also connected to the bottom outlet of the Silicone/IPA tank mixture. This is the inlet flow port.
- 2.6 The tubing that is attached to the upper end of the module is connected to the outlet on the lid of the tank. The end of the tubing must be above the level of the solution liquid polymer. This is the outlet flow port.
- 2.7 Use a peristaltic pump to circulate the polymer mixture through the KrosTrac module at a pressure of 5 psi for two minutes.

### 3.0 Procedure for removing the excess liquid polymer from the modules:

- 3.1 Attach the coated module to the manifold.
- 3.2 Apply a vacuum source for approximately 30 minutes to remove the excess polymer or use clean compressed air at 5 LPM for 30 minutes.
- 3.3 Use IPA to remove any liquid polymer from the exterior surface of the module.

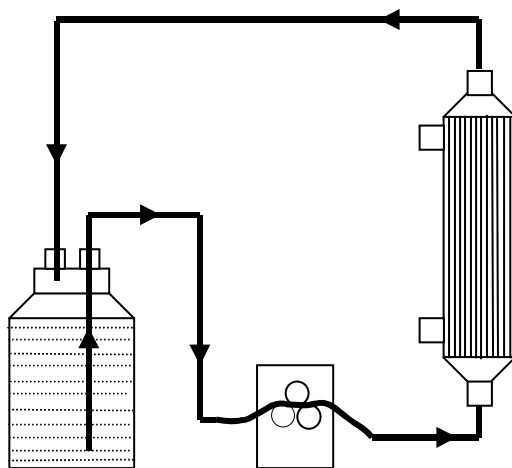
#### 4.0 Module Pressure test:

- 4.1 Close one port on the module that has been impregnated with liquid polymer using a 1 1/2" sanitary block cap.
- 4.2 Connect the rubber bulb pressure tester to the other port of the module.
- 4.3 Apply a pressure of 160 mmHg (3.1 psi) by squeezing the rubber bulb hand pump.
- 4.4 Release the bulb, close air valve and watch the gage.

Pass: If the pressure indicator slowly rotates counterclockwise (10 mmHg in approximately 10 seconds), the polymer has completely filled the membrane pores and the unit has passed the test.

Fail: If the indicator immediately drops to "0", the liquid polymer has not completely filled the membrane pores. A higher "leak down" rate indicates that air is leaking through the pores and the module has failed the test.

#### SCHEMATIC DIAGRAM OF THE SET UP



**Figure A-1**  
**Schematic Diagram of the Set Up**